Master Thesis, Department of Geosciences

Stabilization of metals and metalloids in contaminated shooting range soils – the effect of iron-based amendments

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Abstract

Shooting range soils contain large amounts of copper (Cu), zinc (Zn), lead (Pb) and antimony (Sb) from spent bullets. They are sources of contamination for soil, groundwater and surface water, and may pose a risk to the environment and human health. The investigated shooting range at Steinsjøen (Hurdal, Norway) has surface and porewater concentrations exceeding EU drinking water limits and Norwegian environmental quality standards. Chemical stabilization with iron-based soil amendments has shown to be a promising method for sustainable remediation.

A test field was set up at a shooting range bullet trap at Steinsjøen. The aim was to investigate the long-term retention effects of two different iron-based amendments. Different sections with reference soil (no amendments), soil with CFH-12&limestone (ferric oxyhydroxides and limestone for pH regulation), and soil with zerovalent iron (Fe) were established. Some sections contained 2%, some 4% amendments mixed in, and some contained amendments as top application (2%). Porewater samples were taken from July 2010 to October 2013 and analyzed. In addition, surface water was sampled in 2013.

Examination of reference soil porewater indicated a constantly high weathering rate of spent bullets with high concentrations of Cu, Zn, Pb and Sb. The results showed that pH and DOC levels play important roles in element mobilization. Both amendment types showed good retention for Pb (>94%) in all soils with mixed in application. Antimony (59-74%), Cu (64-70%) and Zn (60-73%) retention in soil mixed with 2% CFH-12&limestone was lower than for Pb. The same was valid for Sb (~73%) and Cu (46-94%) in soil mixed with zerovalent Fe. Zinc retention was very low in the zerovalent Fe amended soil, even negative (-26-26%), probably due to a lower pH than in soil with added limestone and small Zn concentrations in the amendment itself. When adding 4% amendment, a retention improvement was only found for Sb (>85%). Top application did not show good results for any of the elements due to no downward movement of sorbents and had negative effects on cation retention in CFH-12&limestone treated soil probably due to ion exchange reactions with calcium (Ca).

Geochemical modeling with Visual MINTEQ showed that approximately ~20% Pb was bound to fulvic acids containing phenolate (FA2) and ~70% of the Cu to fulvic acids containing carboxylate (FA1) in the reference soil. 100% of Pb and Cu in porewater from CFH-12&limestone treated soil formed complexes with fulvic acids, most (>90%) of which was FA2. This change in Cu speciation is probably due to increased pH. Zinc occurred primarily as freely dissolved Zn^{2+} and Sb aspentavalent $Sb(OH)_6^-$. Modeled saturation indices indicated element undersaturation and no precipitation of secondary minerals.

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Content

Abbreviations

Al	Aluminum
Ca	Calcium
CFH-12	Ferric oxy-hydroxide produced by Kemira
Cu	Copper
DOC	Dissolved organic carbon
EC	Eletrical conductivity
EU	European Union
FA1	Fulvic acids with carboxylate
FA2	Fulvic acids with phenolate
Fe	Iron
ICP-MS	Inductively coupled plasma mass spectrometry
Mn	Manganese
mV	Millivolts
NGI	Norwegian Geotechnical Institute
Pb	Lead
Sb	Antimony
SFT	Statens forurensningstilsyn
SI	Saturation index
TOC	Total organic carbon
XRD	X-ray diffraction
Zn	Zinc
μS/cm	Micro siemens per centimeter

1. Introduction

Heavy metals and metalloids are increasingly found in the environment. Shooting ranges are major sources of copper (Cu), zinc (Zn), lead (Pb) and antimony (Sb). Higher concentrations have been found in nearby groundwaters[1] and streams draining shooting ranges.[2, 3] Usually, these areas are located far away from human settlements, but as these grow, the distance decreases, and the shooting ranges become abandoned and used for other purposes. Contamination from these areas may pose a potential threat to human health, especially when the runoff infiltrates to aquifers used as drinking water sources. In Switzerland, health threats from shooting ranges are caused by their close vicinity to agricultural land where contaminants are taken up by crop plants.[4, 5]

The source of the contaminants are spent bullets, which primarily contain Pb (~90%) and smaller amounts of Sb, arsenic (As), cadmium (Cd), Cu, nickel (Ni) and Zn.[6, 7, 8] The bullets are exposed to weathering, releasing these elements into the soil and porewater. Mobilized contaminants in solution may leach into the groundwater and be made available for plants[9]. In Norway an estimated 103t Pb, 73t Cu, 12t Zn and 12t Sb were deposited at military and civil small arms ranges in 2006.[2] Most of the bullets end up in the stop butt zones, but many are distributed widely on the whole range[7] which represents a challenge to find long-term remediation methods for these sites.

Chemical stabilization of contaminants is a promising method to deal with polluted areas. It may be applied on site, making it possible to reuse the area. Soil amendments using iron-based sorption materials have been shown useful for immobilizing Pb, Cu, Zn and Sb. Weathering of bullets and metal mobilization under natural conditions may occur over a long period, and the sorption capacity of added amendments may decrease or change.

Knowledge is lacking about the long-term success of chemical stabilization through soil amendments. The work of this thesis is part of the long-term study on the effectiveness of the amendments CFH-12 and zerovalent Fe in a field experiment on an abandoned shooting range at Steinsjøen in Norway. The original study by Okkenhaug et al. (2013) investigated the Sb sorption capacity of these Fe-based amendments with no soil, their Sb immobilization efficiency when mixed with shooting range soil and liming agents in batch tests, and Sb retention of the treated soil in column leaching tests[2]. The aim of this paper is to evaluate the conditions under which Pb, Cu, Zn and Sb are sorbed best. The amendments must be in good

contact with the contaminants for best results. This requires the correct application method, and two types, sorbents mixed into the soil and top application, are tested in the Steinsjøen shooting range test field. For a long-term stabilization it is important to find out if and when the metals will be mobilized again.

1.1 The test field at Steinsjøen

The test field is located on shooting range no. 4 at Steinsjøen, about 12 km north of Hurdal in the Northern part of the Oslo rift which stretches in a SSW-NNE direction (Fig. 1.1-1). This part of the Oslo rift consists primarily of batholiths which are mostly syenitic rocks and alkaline granites and probably the host rocks for the investigated soil.[10] Because these rocks have substantially lower heavy metal content, the high concentrations in the shooting range soil are not connected to the geology of the area. A small creek drains the shooting range and flows into the lake Brenntjernet and eventually into Norways largest lake, Mjøsa.

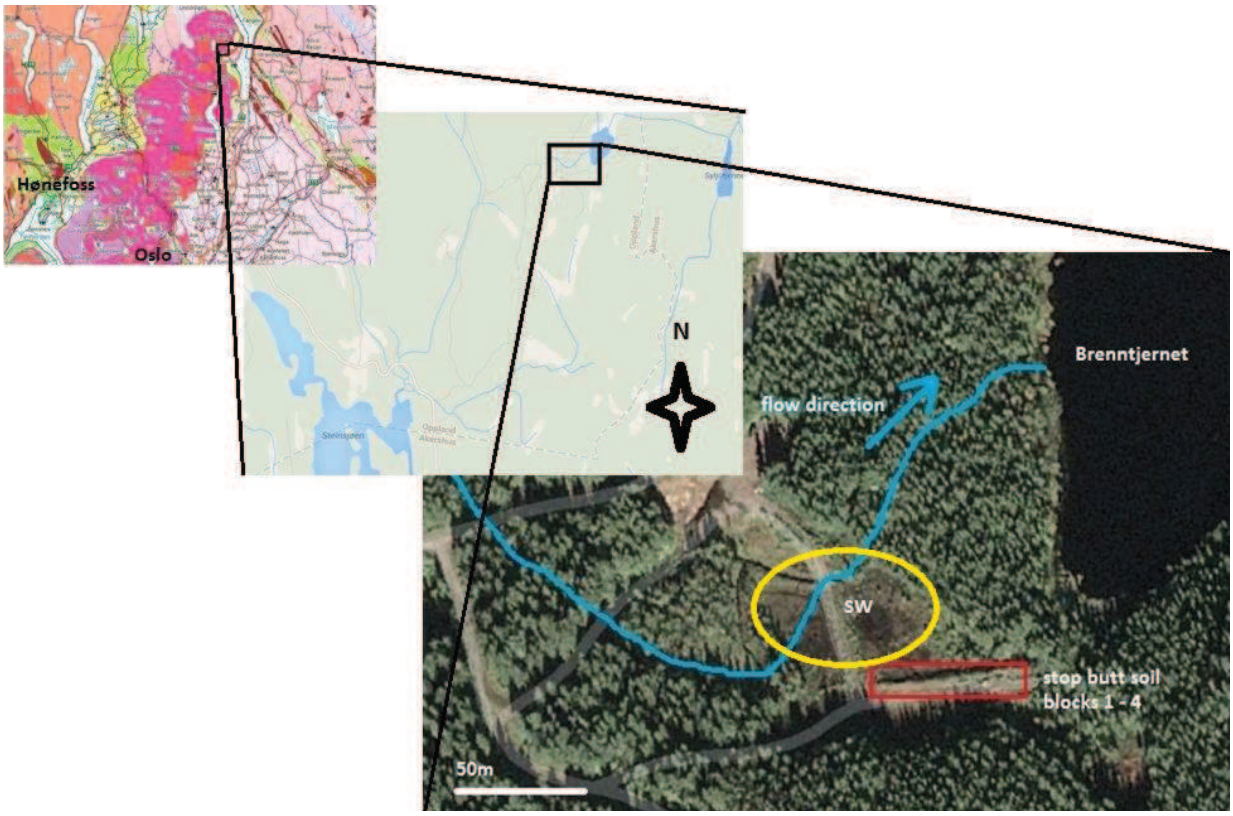

Figure 1.1-1: Top left: The location of Steinsjøen shooting range no. 4 in the Oslo rift (the purple area stretching from Oslo to Steinsjøen in a SSW-NNE direction[11]. The other two maps are modified from google maps. Surface water samples were taken from the yellow area (SW).

The test field at Steinsjøen was established in 2010. Four blocks (block 1-4) with three sections (A, B, C) each were installed at the site. The blocks were filled with bullet trap soil mixed thoroughly with a sorbent (Fig. 1.1-2 and Table 1.1-1). The first section (A) of each block contains the reference soil (no sorbent), the second (B) is filled with soil mixed with iron hydroxides (CFH-12) and limestone for pH regulation, and the third section (C) is soil mixed with zerovalent iron. Blocks 1 and 3 contain soil with 2% sorbent material mixed in, block 4 with 4%. In block 2, the sorbents were used in a top application, also 2% of the total soil in the section.[2] In every section, six Rhizon samplers (see chapter 3.2) were installed, two on the North-Western side of the section (samplers 1 and 2), and four on the South-Eastern side (samplers 3 and 4 on the top, 5 and 6 on the bottom, see Figures 1.1-2 and Table 1.1-1).

Figure 1.1-2: The test field at Steinsjøen. Left: Blocks 1 to 4 with sections A, B, C each. Right: Syringes attached to rhizon samplers to extract porewater.

Application	mixed in			top application		
Block	1			2		
Section	A	B	C	A	B	C
Soil	reference	2% CFH-12 & 1% limest.	2% Fe grit	reference	2% CFH-12 & 1% limest.	2% Fe grit
Application	mixed in			mixed in		
Block	3			4		
Section	A	B	C	A	B	C
Soil	reference	2% CFH-12 & 1% limest.	2% Fe grit	reference	4% CFH-12 & 2% limest.	4% Fe grit

Table 1.1-1: The Steinsjøen test field: Blocks 1-4 with sections A-C. The amendments in block 2 are applied on top, not mixed in. The amendment concentration in block 4 is twice as high as in the other three blocks.

2. Theory

The stabilization of contaminated soil by adding chemicals is dependent on several different factors, namely the element properties of the contaminants (described in chapter 2.1), the amendments (chapter 2.2) and several soil processes (chapter 2.3).

2.1 Element properties

In this chapter, relevant properties of lead, copper, zinc and antimony are presented in order to give an overview over their chemical behavior in soils. The first three are usually present as cations, whereas antimony occurs primarily as an oxyanion. In general, higher pH favors cation sorption, whereas low pH favors anion sorption. In addition a brief description of the element toxicity is given.

Lead (Pb)

The toxicity of lead is characterized by growth damages in plants and a constraint in microbial activity in the soil. In humans, lead accumulates in the liver, kidneys and bones. Once taken up by the organism, it stays in the body for a relatively long time (5-20 years) and thus can be accumulated easily. Average Pb background concentrations in soil range typically from 2–60 mg/kg.[12]

Pb solubility is influenced by pH, total Pb concentration, organic matter content and redox conditions. The lower the pH, the higher is Pb solubility. In general, Pb has a low solubility at pH > 5, but the presence of dissolved organic carbon (DOC) increases it. Above pH 7, Pb is usually only present in solution when complexed with DOC.[12]

Pb is, compared to other heavy metals, less mobile, and its affinity to Fe-, aluminum (Al)- and manganese (Mn)-oxides is very high. With pH levels > 5, most Pb (75 – 85%) in a soil is sorbed to these oxides. An increased amount of solid organic matter reduces Pb mobility as well. At lower pH levels (< 4), Pb is predominantly sorbed to soil organic matter (up to 80% of all Pb) instead of the metal oxides mentioned above. The amount of Pb sorbed to clay minerals depends on the mineral type and other soil factors, but is usually between 1 and 25%.[12]

Copper (Cu)

Copper is important for life. It is toxic in high doses for plants and some animals, but no chronic Cu toxicity has been observed for humans.[12]

In natural conditions its occurrence depends on the soil composition. Below a pH of 6, it is primarily bound to soil organic matter. Above this value, Cu is mainly bound to Mn- and Fe-

oxides and to some extent to clay minerals. At a pH > 5, Cu is usually not exchangeable. The solubility of Cu in acidic forest soils with low pH is much higher. At high pH values (> 5.5), the amount of mobile Cu that forms complexes with DOC increases rapidly and reaches usually 100% at pH > 7 (like Pb).[12]

Zinc (Zn)

Zinc is an essential trace element for plants, animals and humans. There is now known chronic Zn toxicity for humans, but Zn has negative effects on plants and microorganisms in soils with very high Zn concentrations. Zinc is primarily bound to soil organic matter from pH 5-7. Above pH 7, Zn is mostly sorbed to Mn-, Fe-, and Al – oxides, especially in soils with a very high Zn concentration. In soils with pH < 5, the affinity of Zn to the oxides and humic acids decreases, and Zn is primarily bound to silicates. Most of the Zn in solution is bound to DOC at pH > 6.5.[12]

Antimony (Sb)

Antimony is a toxic element which can cause serious health problems already in very low doses. Sb exhibits mainly two oxidation states, Sb(III) and Sb(V), of which Sb(V) is less toxic. In bullets, Sb is used as a hardener, and thus contributes to shooting range pollution. Sb is a metalloid and behaves differently than the heavy metals discussed above. Under environmentally relevant pH conditions, Sb(III) and Sb(V) occur as the neutral $Sb(OH)_3$ (antimonite) and the oxyanion $Sb(OH)_6^-$ (antimonate), respectively. Antimonite is predominant in reduced, antimonate in oxidized soils.[13] According to Scheinost et al. (2006), the weathering of bullets in shooting range soil produces mainly Sb(V), meaning that Sb occurs as anionic $Sb(OH)_6^-$.[14] This suggests a sorption behavior opposite to that of the cations. Like cations, both Sb(III) and Sb(V) are sorbed by Fe-oxides and Fe-hydroxides[15, 14]. Sb(V) sorption mainly occurs at lower pH (< 7)[15]. Another substance influencing Sb sorption is DOC. DOC is a potential competitor of Sb for sorption sites. Experiments show that Sb mobility increases with DOC concentration[13].

2.2 Chemical stabilization as a soil remediation method

Awareness of soil contamination as a problem for human health and the environment arose in the 1970s. Since then, contaminated soil was treated mainly by incineration or containment, which could be done in situ, by excavating and containing it on the site, or by removing and transporting it to a landfill for containment. These methods are not sustainable, and some are

very costly. As soil is a valuable, but depleting resource, removing and sealing it off somewhere else is not a good way of handling contaminated soil. New sustainable strategies where soil can actually be reused need to be identified. It is also important to have different approaches to each scenario, because the problem changes depending on the type of contamination, the scope and the intended use of the land. Sustainable remediation therefore requires a method that will make a contaminated site reusable for the long-term future. This is done by either removing the source of the contaminants, meaning that they are taken out of the soil, or by immobilizing them. Immobilization leaves them in the soil, but in a state in which they are not available for transport or plant uptake. This entails precipitation or adsorption.[16]

Promising is the chemical stabilization through soil amendments. This process does not require removal of the soil, and the methods are generally relatively cost efficient, depending on the amendment type. Commonly used have been clay minerals, zeolites and activated carbon, but these are not very economical. Lime, phosphates, hydroxides, oxides and zerovalent iron belong to the group most studied.[17] A few methods will be presented here briefly.

Organic matter has a high potential for soil remediation, and is readily available as organic waste. Organic waste is able to change the soil in several different ways. It has large sorption surfaces where metals can be adsorbed and immobilized, it promotes mineral precipitation by increasing the redox potential through aeration and pH changes (slight increase). The problem associated with this is mobilization of metals through complexation with DOC which is contained in organic waste. In addition to that, organic waste derived from populated areas tends to contain higher amounts of contamination itself.[18]

Adding limestone to the soil increases the pH which benefits the sorption of cations. This method has been used at Finnish shooting ranges, but proved to be counterproductive.[5] While immobilizing the heavy metals such as Pb[19], Cu and Zn, Sb was mobilized. Raising the pH by adding lime stone is a powerful tool for binding cations, but raising the pH of acidic forest soils mobilizes naturally occurring Sb and substantially increases the Sb concentration in soil water.[5]

Phosphate (P) soil amendments aim at immobilizing divalent cations such as Pb^{2+} by adding a highly soluble phosphate mineral to the soil, and precipitating more insoluble, Pb-bearing phosphates. An example is the addition of $Ca_5(PO_4)_3OH$ (hydroxyl-apatite) which dissolves, and the precipitation of $Pb_5(PO_4)_3Cl$ (pyromorphite).[17] Phosphates such as diammonium

phosphate and calcium dihydrogen phosphate have been experimented with by Spuller et al. (2007). In batch experiments using soil taken from a shooting range, the phosphates showed good results in stabilizing Pb, but mobilized Cu and Sb to such a degree that phytotoxicity was even higher in the treated than in the reference soil.[20] It is likely the result from competition between Sb and phosphates for the same sorption sites. Like Pb, Zn was also immobilized by phosphate amendments[21]. Kilgour et al. (2008) conducted several tests with phosphate-based fertilizers. The soils were taken from shooting ranges with high Pb and Sb concentrations. The bioavailability of Pb decreased significantly, but an initial pH drop after addition of the phosphate suggests Pb leaching further into the groundwater in the beginning of remediation. Also, the mobility of arsenic (As) and Sb, which have a similar behavior increased due to the amendments. Naturally occurring elements, such as As, are mobilized that are not linked to the contamination (here bullets).[22, 23] This gives additional reason to question the usefulness of phosphates as soil amendments. Another risk of using this amendment type is the leaching of phosphate into downstream water bodies where it may cause eutrophication[17].

The use of oxides and hydroxides, especially Fe-(hydr)oxides shows very good sorption results for the elements Pb, Cu, Zn and Sb[21, 2], although pH changes due to the amendments need to be taken into account and regulated.[21] Shooting range soil batch experiments showed good retention of Pb, Cu and Sb with the addition of goethite and deferrisation sludge.[20] Another phosphate amendment is 5% Buffer Block® calcium phosphate, which was used in experiments conducted by Griggs et al. (2011). This material contains phosphate, but also small amounts of Al-hydroxide, counteracting Sb mobilization induced by competition of the anionic phosphate.[23] This shows that, depending on soil and contaminant composition, the best combination of different amendment types needs to be chosen.

Good results have also been obtained in column leaching tests with CFH-12 and zerovalent Fe by Okkenhaug et al. (2013)[2]. CFH-12 is a product consisting of Fe-hydroxide. It reduces the pH of the soil water leading to heavy metal leaching which was counteracted by the addition of limestone resulting in very good heavy metal and metalloid retention. Zerovalent Fe showed good results as well, although Sb retention was overall lower with this than CFH-12. In the beginning of the test, retention was low, but increased with time. This was attributed to the Fe reacting to form Fe-hydroxides which have a much higher sorption capacity than elemental Fe.[2] Secondary mineral formation is generally the best way to stabilize contamination. Sorption to mineral surfaces is highly susceptible to changes in the soil.

Minerals are more stable and therefore preferable over sorption. The minerals that are expected to form with Fe-based remediation are (hydro)carbonates, (hydr)oxides and anglesite ($PbSO_4$). A study done on shooting range soil in Florida, USA, showed that hydrocerussite ($Pb_3(CO_3)_2(OH)_2$) formed as a crust on weathered bullets and in stop butt soils with higher pH. In soils with lower pH hydrocerussite, cerussite ($PbCO_3$), massicot (PbO) were detected as bullet crusts, but not in the soil.[24] Other expected minerals are Cu carbonates (cuprite (Cu_2O), malachite ($Cu_2CO_3(OH)_2$) and azurite ($Cu_3(CO_3)_2(OH)_2$)), smithsonite ($ZnCO_3$), oxides (tenorite (CuO), $Zn(OH)_2$, massicote (PbO), $Pb_2O(OH)_2$, SbO_2).

A number of other stabilization experiments have been conducted. In the following are mentioned two examples which show the variety of amendment possibilities. The first is scoria, a vesicular volcanic rock (similar to pumice, but denser), which was tested, resulting in effective and cost efficient sorption of Zn(II).[25] The second example is an experiment with different combinations of five organic matters, three phosphate compounds, and zerovalent iron grit. In this study, the retention of Cu in topsoil was tested by growing beans, and the results were generally positive with one combination even enhancing plant growth.[26]

2.3 Important soil processes and parameters

There are a few key soil processes which shall be presented briefly.

2.3.1 Kinetic and equilibrium reactions

For any type of reaction it is essential to know the concept of kinetic reactions and chemical equilibrium which are based on the law of mass action:

$$cC + dD = yY + zZ \qquad (2.3.1\text{-}1)$$

C and D are ions which react to produce ions Y and Z. The lower case letters represent the amount in moles. The distribution of reactants and products in equilibrium is described by the equilibrium constant K.[27]

$$K = \frac{(Y)^y(Z)^z}{(C)^c(D)^d} \qquad (2.3.1\text{-}2)$$

This equation can be used for systems with low ion concentrations. The equilibrium constant is a known value which can be calculated by thermodynamic principles. At equilibrium, no reactions are taking place because no energy is available, whereas a reaction will take place if

equilibrium has not been achieved.[27]

In solutions with higher ion concentrations, the ions behave non-ideally which requires the use of activities instead of concentrations. The activity of ions changes with ion concentration in a solution and ionic charge. To calculate the activity, an activity coefficient is needed. The basic activity model for calculating the activity coefficient is the Debye-Hückel equation:

$$log\gamma_i = -Az_i^2(I)^{0.5} \qquad (2.3.1\text{-}3)$$

Here, i represents the ion, A is a temperature dependent constant, z is the ion charge, and I is the ionic strength. The ionic strength is a value which describes the total concentration of an element according to its ionic charge (z). For species with a charge higher than one, the impact on the activity coefficient is larger. The basic Debye-Hückel equation is limited to solutions with an ionic strength of I = 0.005M which is fresh groundwater. For less dilute solutions with a higher ionic strength of up to 0.1M, the extended Debye-Hückel equation can be used. It adds another temperature-dependent parameter (B) and the radius of the ion. For solutions with an ionic strength of up to 20M, the Davies equation provides accurate values for the activity coefficient. The Davies equation incorporates additional correction parameters and can be used for solutions with a very high salinity.[27] The Davies equation was used for speciation in Visual MINTEQ.

2.3.2 Saturation

It is helpful to find the saturation of a contaminant to show whether precipitation of secondary minerals plays a role in the retention. The most likely secondary minerals are Fe-minerals, oxides and carbonates. Equilibrium is always the distribution of ions with respect to a solid mineral which they form. In open systems, such as a soil with the occasional input of rainwater, the rainwater constantly reacts with the solids of the soil. Some minerals will react quickly and achieve equilibrium relatively fast, others will be slower. This creates a complex solution which is referred to as a partial equilibrium system. A solution which has not reached equilibrium with a solid phase will not give the equilibrium constant K of equation 2.3.1-2 as a result, but a value differing from K. This is the ion activity potential (IAP):

$$IAP = \frac{(Y)^y(Z)^z}{(C)^c(D)^d} \qquad (2.3.2\text{-}1)$$

The ratio IAP/K determines the distance of a solution from reaching equilibrium. It describes its saturation state: a solution is undersaturated with respect to the involved minerals, when IAP/K < 1, and supersaturated when IAP/K > 1. The IAP and K can also be used to determine the direction of the reaction. If IAP > K, [C] and [D] increase while [Y] and [Z] decrease. If IAP < K, it is the other way around.[27] [C], [D], [Y] and [Z] are the activities of ions C, D, Y and Z. Saturation indices were modeled with Visual MINTEQ to determine saturation of possible precipitants.

2.3.3 Acid-base reactions

Acid-base reactions are important because they deal with the transfer of hydrogen ions (H^+) from and to other ions which influences the pH. The pH strongly affects the amount of dissolved cations water is able to take up. At low pH, the amount is larger than at high pH. [27]

2.3.4 Dissolution and precipitation reactions involving salts and liquids

Dissolution and precipitation reactions involving salts and liquids are not dependent on the hydrogen ion and are therefore not called acid-base reactions. They are the reason for the mobility of contaminants. With water having a positive charge on one side, and a negative one on the other, the solubility of polar compounds is very good. A charged ion (Pb^{2+}, Cu^{2+}, Zn^{2+}, $Sb(OH)_6^-$) will be easily taken up into the water, because it is able to attract one end of the polar water molecule and repel the other. It is incorporated into the structure of the water, rearranging the water molecules in such a way, that they group around the charged ion according to the attraction of the charges involved.[27]

2.3.5 Complexation reactions and speciation

Complexation reactions are reactions forming complexes of ions with other ions or molecules. The central ion is the cation, often a metal that forms complexes with anions. The anions, also referred to as ligands, that are typically found in groundwater are Cl^-, F^-, Br^-, SO_4^{2-}, PO_4^{3-} and CO_3^{2-}.[27] Dissolved organic carbon (DOC) is also an important ligand. For some of the samples from the Steinsjøen shooting range, DOC, Cl^- and SO_4^{2-} concentrations were measured and used for modeling with Visual MINTEQ. Complexation is important because it increases the mobility of metals and their transportation from contaminated soil into the groundwater. Metals not in a complex are usually not as mobile because of sorption by clay minerals or precipitation which is pH-dependent. The higher the pH, the closer a metal in a fluid is to saturation with respect to its solid phase, but even at higher pH values, metal mobility can be significant due to complexation.

In a solution, a metal is likely distributed among different complexes. The stabilities of these

complexes can be used for speciation. Since the complexation reaction is usually fast, several mass action equations can be used in a row. It is easier to use association reactions for this purpose.[27] In the following example there are complexation reactions with their corresponding association reaction to the right:

$$Pb^{2+} + OH^- = Pb(OH)^+$$
$$Pb(OH)^+ + OH^- = Pb(OH)_2$$

$$Pb^{2+} + OH^- = Pb(OH)^+$$
$$Pb^{2+} + 2OH^- = Pb(OH)_2$$

The equilibrium constant of an association reaction is called the stability constant (β):

$$\beta = \frac{(Pb[OH]_2)}{(Pb^{2+})(OH^-)^2} \qquad (2.3.5\text{-}1)$$

Larger values for β correspond to a more stable complex. The complexation in the above example is pH-dependent as the ligand is $(OH)^-$. The method above can also be implemented when the ligands are different, for example:[27]

$$(Pb)_{total} = (Pb^{2+}) + (PbCl_2) + (PbCl_3^-) + (PbOH^+) + (PbCO_3)$$

Equation 2.3.5-1 describes the basic principle to calculate the stability of many different complexes, or species of a given element such as Pb. Knowing the stability of each Pb species will indicate the species distribution of Pb in percent.[27]

2.3.5 Surface reactions

Surface reactions are reactions between ions in solution and the surrounding material. When a solution is mixed with solids (for example sediments), mass partitions between the liquid and the solid. A certain amount of ions in the solution are sorbed to the solids surface until reaching equilibrium, when allowed.[27] The amount sorbed is dependent on the amount of surfaces available, the sorption capacity of the surface (mineral type), sorbed element properties and pH.

2.3.7 Ion exchange reactions

Ion exchange reactions can change the chemistry of groundwater drastically. Cations and anions are often bound to mineral surfaces. This bond is not very strong and can easily be broken. Thus, ions in solution can exchange places with bound ions. An example of this is the exchange of Cu and Pb:

$$Pb^{2+} + \text{Cu-clay} = Cu^{2+} + \text{Pb-clay}$$

The exchange can take place because of negatively (or positively for anions) charged mineral surfaces. Mineral exchange sites prefer certain ions over others, in this example Pb over Cu. A sequence is hard to establish, but a tendency in preference of ions with a higher charge has been seen. Most common are negatively charged surfaces so that the cations are prone to sorption. The reasons for charged surfaces are imperfections or the substitution of elements in the structure of the sorbing mineral. A good example is Al^{3+} substituting Si^{4+} (silicon). This results in an overall negatively charged surface of the crystal. The most important group of minerals acting as exchangers comprises the clay minerals. They have a high ion exchange capacity (CEC).[27]

Kaolinite, metal oxides (i.e. SiO_2, Fe_3O_4) and metal oxyhydroxides (i.e. FeO(OH)) represent another group of exchangers. The Fe-based amendments used in the Steinsjøen test field described in this paper are such exchangers. Their surface charges change with the groundwater composition and depend on pH. At low pH, more H^+ ions (i.e. $Fe(OH)^+$) are bound to those surfaces facilitating the sorption of anions. At high pH, Fe species with negative charges are dominant, and cations are sorbed. There is a pH value in between, where the surface exhibits no charge. This is the zero point of charge (pH_{zpc}), or isoelectric point and it is unique for each mineral.[27]

2.3.8 Redox potential

Eh is referred to as the redox potential. It describes the electron activity and is a measure for the amount of redox reactions taking place. The redox potential E_H (in volts) is a measured value. The negative logarithm of the electron activity is called pe and is connected to Eh in the following way:

$$E_H = \frac{2.3\ RT}{F} pe \qquad (2.3.8\text{-}1)$$

F is the Faraday constant (electrical charge of one mole of electrons). The term 2.3RT/F equals 0.059V at 25°C.[27] A fixed value for Eh was taken from a Eh-pH diagram (stability of Sb species) by Okkenhaug et al. (2012)[28] and used in Visual MINTEQ.

3. Materials and methods

3.1 Amendments

The amendments CFH-12 and zerovalent Fe-grit were used for chemical stabilization of heavy metals and metalloids at the test field at Steinsjøen, Norway. They are both Fe-based, and Pb, Cu, Zn and Sb have a high affinity to Fe and Fe-(hydr)oxides.

CFH-12 powder

CFH-12 powder is a ferric oxyhydroxide obtained from the chemical company Kemira, Norway. It has a Fe content of ~42% and a small amount of Zn (Table 3.1-1). Upon mixing shooting range soil from Steinsjøen with 2% CFH-12 in a column leaching experiment by Okkenhaug et al. (2013), a pH drop in the leaching solution was measured resulting in mobilization of heavy metals.[2] Therefore, limestone (from Franzefoss Minerals AS, Norway) was added to counteract this trend, and the results were positive. Despite the higher pH, Sb retention was still very good (between 89 and 98%). The retention for the three heavy metals mentioned above varied between 49-97% for Pb, 47-95% for Cu, and 36-100% for Zn.[2] CFH-12&limestone was applied to the B sections of the Steinsjøen test field blocks.

Zerovalent Fe-grit

The Fe-grit (0.3-1.0 mm) from Gotthard Mayer, Germany, has a Fe content of ~92% and a small amount of Cu (Table 3.1-1). The elemental Fe has fewer sorption sites than Fe (hydr)oxides. A column leaching test with Steinsjøn shooting range soil and 2% Fe-grit mixed in indicated weak sorption of Sb at the start. Towards the end, at approximately pore volume number 300, the soil reached Sb retention of 70%. An increase of sorption with time was also measured for Pb, Cu and Zn. This is an indication for the need of the elemental Fe to oxidize before good retention can be achieved.[2] Zerovalent Fe was added to the C sections of the test field at Steinsjøen.

	CaO %	MgO %	Fe g/kg	Cu mg/kg	Zn mg/kg	Pb mg/kg	Sb mg/kg
Limestone	55	0.4	0.34	<1	5.3	<10	0.08
CFH-12	-	-	423	6.0	352	<10	0.06
Fe^0	-	-	920	3029	31	2	19

Table 3.1-1: Amendment composition.

3.2 Water sampling

Porewater from each block and section was sampled every year from 2010-2013 in the period May-November. The number of sampling campaigns varied between three and four per year from 2010-2012 (311 samples). Water sampling in 2013 comprises in total five sampling campaigns from the end of May to the end of October (147 samples), with approximately five weeks in between each. The total number of samples was 458.

To extract the porewater from the soil, "Rhizon Soil Moisture Samplers" produced by "Rhizosphere Research Products" were installed in 2010 by the NGI (Norges Geotekniske Institut) at 0.3–0.6 m depth.[28] These samplers have not been removed and were used for sampling in 2013 as well. The properties of the Rhizon samplers are as follows: They include inert material with no ion exchange capability and no adsorption. The mean pore size in the samplers is 0.15 µm which requires no further filtration of the water before the analysis in the laboratory. On every sampling campaign, a syringe was attached to each sampler for two nights in a row. The water was then collected in 35 ml-tubes, combining sample no. 1 with 2, 3 with 4 and 5 with 6 of each section (i.e. A1 with A2, B3 with B4, etc.) giving a total of ~36 samples each sampling day. On days with less water in the samplers, this number was smaller. The water was then put into 14 ml-tubes in the lab at NGI in Oslo, conserved with nitric acid (HNO_3) to avoid metal precipitation as Fe-hydroxides, and sent to the laboratory at FFI (forsvarets forskningsinstitutt) for analyzing concentrations of sodium (Na), magnesium (Mg), potassium (K), calcium (Ca), aluminum (Al), manganese (Mn), iron (Fe), copper (Cu), zinc (Zn), lead (Pb) and antimony (Sb).

The rest of the water was used in the lab at NGI to measure pH and electric conductivity (EC). Some of the samples were analyzed at the Norwegian University of Life Sciences (MBU) for their concentration of dissolved organic carbon (DOC).

After averaging the porewater concentrations in each section for each sampling day, the total number of samples from 2010-2013 became 175.

Surface water samples (SW1-SW4) were taken from four parts in the area in front of the stop butt zone in May 2013. The area is saturated with water (like a wetland) with a small creek draining it (Fig. 1.1-1). These samples were analyzed in the same way as the porewater.

3.3 Chemical analysis

The pH and electric conductivity (EC) were analyzed by the author of this paper, using a pH electrode (Inolab level 2, WTW) and an EC electrode (LF538, WTW). The DOC was analyzed at NMBU (Norwegian University of Life Sciences) by a total organic analyzer (TOC-V CPN, Shimadzu Corporation, Japan). The element concentration measurements were carried out by E. Mariussen at the Norwegian Defence Research Establishment (forsvarets forskningsinstitutt) by ICP-MS (inductively coupled plasma mass spectrometry) with the Thermo X-series II from Thermo Scientific.

3.4 Soil samples

In total, six soil samples were taken from blocks 1 and 2, sections A-C. They were crushed and powdered. The X-ray diffractometer (XRD) used was a Philips X'Pert MPD X-ray diffractometer.

The XRD is used for studying the crystal structure of the minerals in the sample and thus identifying the mineral. The XRD uses X-rays with a known wavelength (λ) to measure the angle (θ) at which the beam is reflected. The spacing (d) between the lattice planes in the crystal is unique for each mineral and can reveal what kind of mineral is being examined. The d can be calculated using Bragg's Law:

$$n\lambda = 2dsin\theta$$

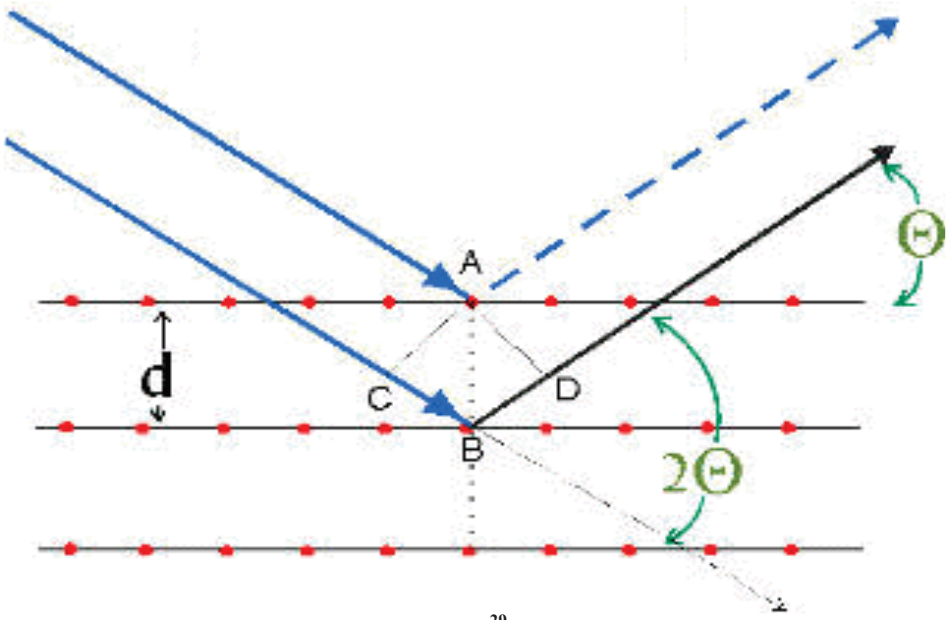

Figure 3.4-1: The principle of Bragg's law[29]. The red dots are atoms and the blue arrows are X-rays. θ is the angle of reflection and d to the spacing between the lattice planes (http://www.helmholtz-berlin.de/forschung/oe/funkma/werkstoffe/methoden/xrd_en.html).

The incoming X-rays are parallel to each other (Figure 3.4-1). When they arrive at the crystal, they interact with the atoms causing radiation to scatter. The X-rays are reflected at the atoms in the lattice planes. Some of them are reflected on the first planes, some at the following planes. The reflected X-rays from the different lattice planes either cancel each other out (destructive interference) or they are emitted parallel to each other again (constructive interference). For constructive interference to happen, the reflection angle θ needs to be such that all of the emitted X-rays travelled a distance that is a multiple of the wavelength. Because of its dependence on the d spacing, this angle is unique for each mineral.[29] The angles of reflection are plotted against the intensity of the reflected X-rays. The unique d spacing corresponds to peaks in the resulting plot. These peaks are compared to a data base containing mineral data to find out the best fit. The sample has to be crushed in order to get as many orientations of the crystal lattice as possible. This increases the likelihood of the lattice to lay in an orientation that will produce any results. Different angles are measured as different sides of the crystal lattice are interacting with the incoming X-rays.

3.5 Geochemical modelling with Visual MINTEQ

The computer program "Visual MINTEQ" by Jon Petter Gustafsson at KTH was used for the speciation of the elements contained in the porewater and saturation of species. The input contained the measured concentrations of the elements and the measured pH (fixed). This was done for sampling campaigns in 2013. For a few dates, the anion concentration of Cl^- and SO_4^{2-} were added. Since the impact of these was found to be insignificantly small, it can be assumed that the data of the other outputs are not false.

Other parameters were alkalinity which was set at 20 mg/L bicarbonate (HCO_3^-) and the redox potential Eh, set at 500 mV. This number was retrieved from Okkenhaug (2013), where an Eh-pH diagram of Sb species is shown[2]. The value of 500 mV lies in the stability field of antimonate ($Sb(OH)_6^-$), where Sb has the oxidation state V. Sb(V) was the only Sb found in porewaters at Steinsjøen[2].

For the DOC, the Non-Ideal Competitive Adsorption (NICA)-Donnan model was used. Since no information on the type of humic acid was acquired, the default value was kept which assumes that 100% of the active dissolved organic matter is fulvic acids. A distinction was made between fulvic acids containing carboxylic (FA1) and phenolic groups (FA2).

For calculating the ionic activity in the solution, the Davies equation was implemented. This is an extension of the Debye-Hückel equation and is better for high ion concentrations.

The output file shows the percentages of each species of the total concentration of an element. The program was also used to examine the saturation indices.

4. Results

Before looking at the results for the treated soil, it is important to look at the original state of the soil without amendments (the reference soil). These results are presented in chapters 4.1 - 4.3. Chapters 4.4 - 4.6 present the results from the treated soil, and chapter 4.7 the results from surface water samples.

4.1 Porewater concentrations in the untreated soil

In the untreated soil, the Sb concentrations showed substantial variation in the porewater in all blocks (Fig 4.1-1). In the months May and June, Sb concentrations were generally lower than in the months from July to September. They decreased again in October. For example, in the year 2011, Sb concentrations in block 1 were 214 µg/L in the end of May, increased to ~295 µg/L in the first weeks of July and September, and decreased in mid-October to 185 µg/L (Fig. 4.1-1). This trend could be seen for each year in the observation period, form 2010 to 2013, indicating a seasonal variation of the concentration of Sb in the soil.

Similar to Sb, the concentrations of the heavy metals Pb, Zn and Cu also showed seasonal variations in the porewater of the reference soil, but they were less distinct, that is there were more exceptions to this trend. For example, the changes for Pb in the year 2012 showed the opposite: the month with the lowest values in all four blocks was August with 270 µg/L Pb (Fig. 4.1-2). In mid-June and end of October, the measured values were as high as 794 and 631 µg/L, respectively.

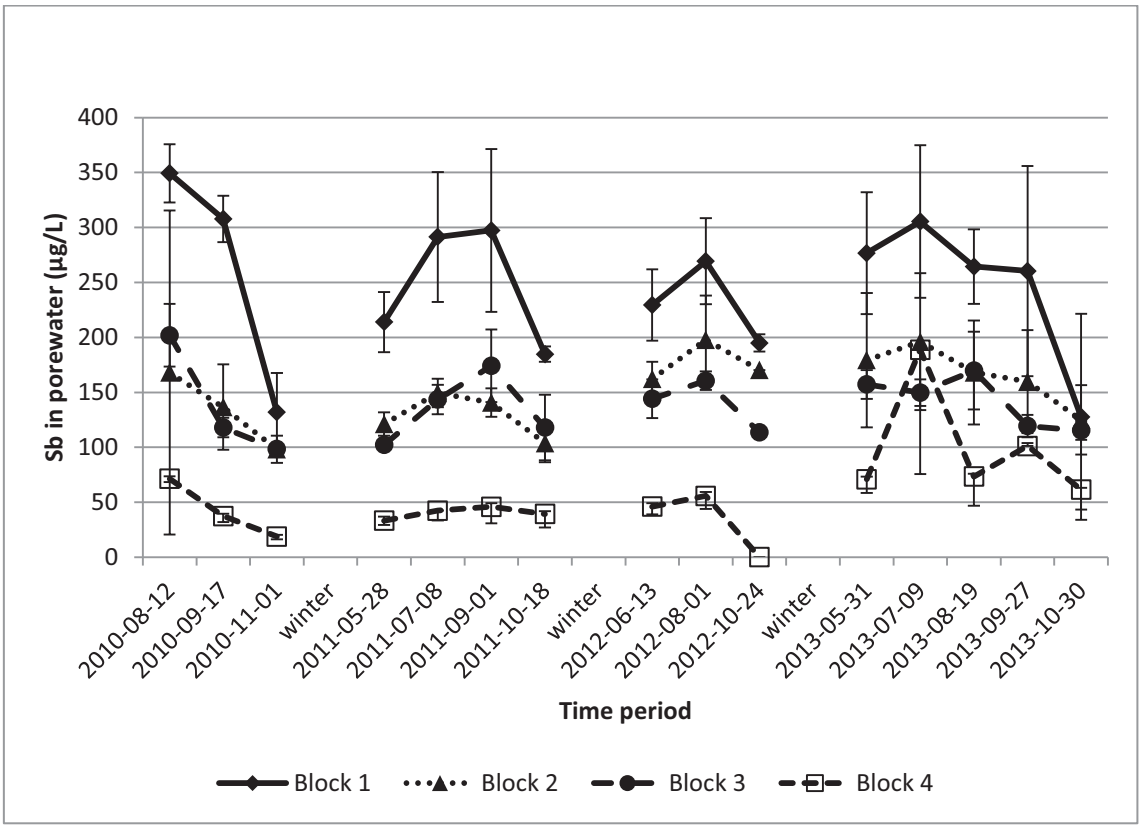

Figure 4.1-1: Antimony concentration in porewater of the reference soil (no sorbent) in all four blocks. The error bars show the standard deviation of three replicates (from 2010-2013).

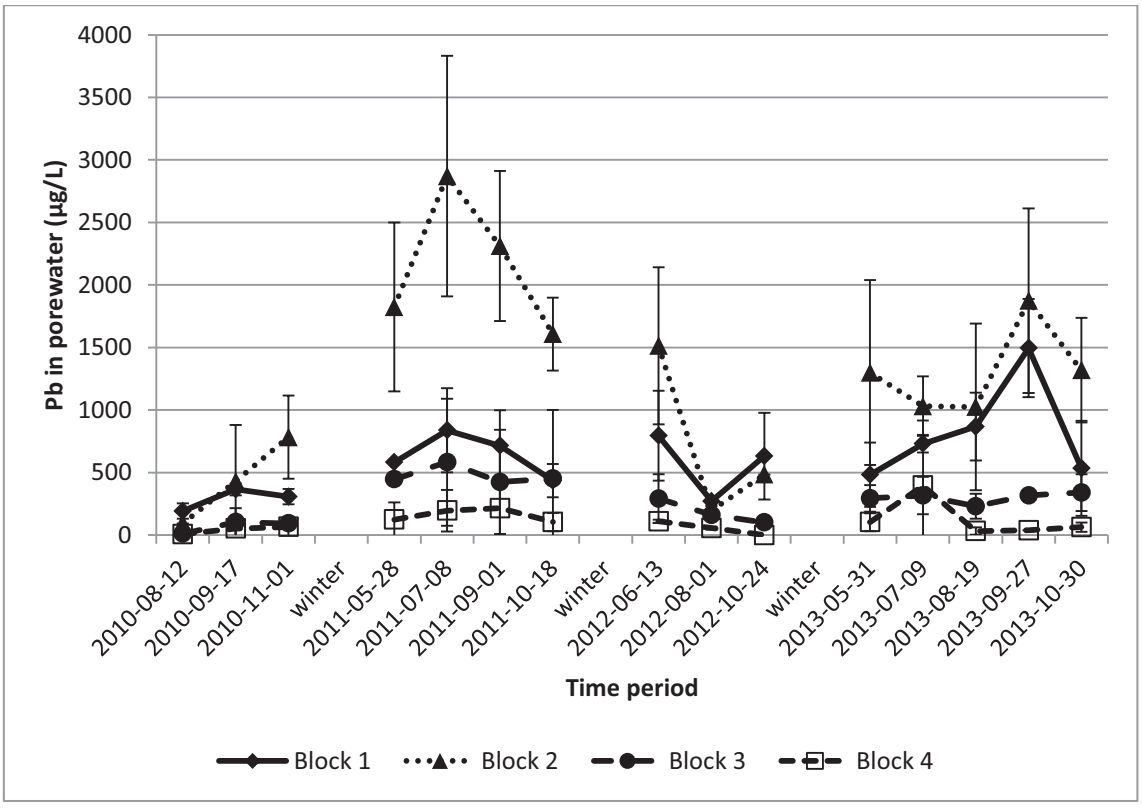

Figure 4.1-1: Lead concentration in porewater of the reference soil (no sorbent) in all four blocks. The error bars show the standard deviation of three replicates (from 2010-2013).

Yearly deviations from the seasonal trend mentioned for Pb concentrations in 2012 could also be found among the blocks. In 2012, while blocks 2-4 matched seasonality, Zn concentrations in block 1 changed from 438 µg/L to 729 µg/l in June and August, and then jumped to 2145 µg/L in October (Fig. 4.1-3). The standard deviation for this point was very high at 2794, much higher than the other two which stayed below 320. It was likely that the high October value was an outlier, because only two samples showed these extremes. Another example for this was observed in 2011. Here, block 2 showed the highest Zn concentration in the end of May, not July or August, while block 1 and 3 clearly followed the trend seen in most other measurements.

The seasonal differences in Cu concentrations were relatively low in most of the blocks, ranging from 37-56 µg/L in block 1, 2011 (Fig. 4.1-4). Higher values were found in block 1 in 2013 and block 2 in 2011-2013, with the highest value for Cu (191 µg/L) in July 2011 in block 2. Seasonal variations were still observable for each block. This means that these variations were independent from absolute Cu concentration.

The concentrations for Pb, Zn and Cu tended to show the same variation as Sb. When Sb concentrations increased, the heavy metal concentrations increased as well. However, in 2011 Cu concentrations behaved opposite, but only in block 4 (Fig. 4.1-4). The values were very low and ranged only from 2 – 16 µg/L.

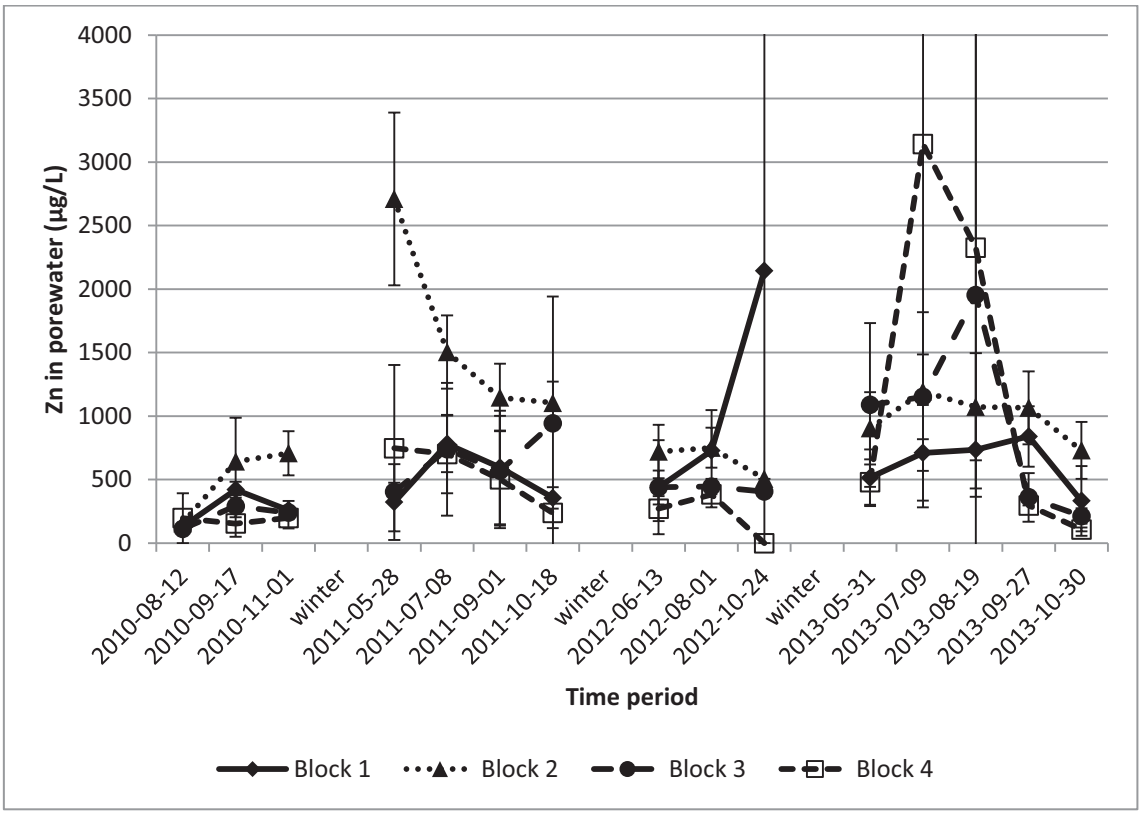

Figure 4.1-2: The zinc concentration in the porewater of the reference soil (no sorbent) in all four blocks. The error bars show the standard deviation of three replicates (from 2010-2013).

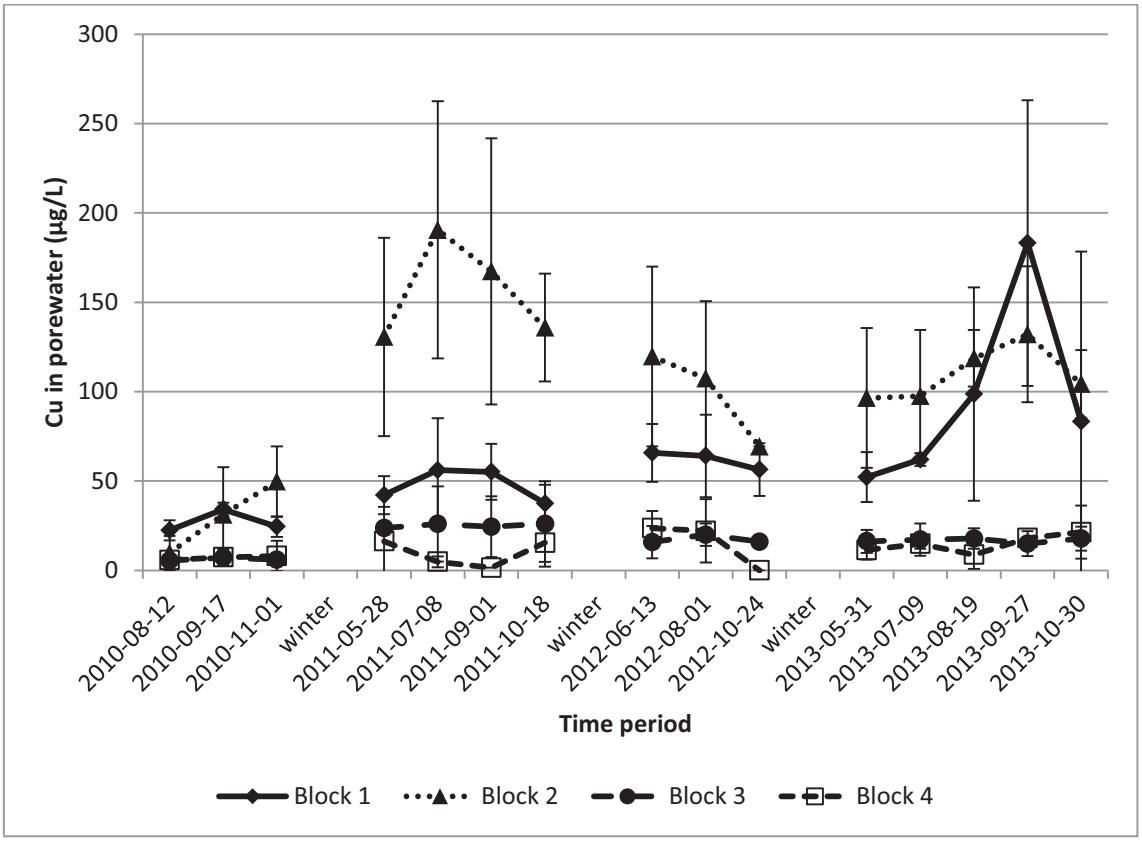

Figure 4.1-4: The copper concentration in the porewater of the reference soil (no sorbent) in all four blocks. The error bars show the standard deviation of three replicates (from 2010-2013).

4.2 pH in untreated soil

The pH of the porewater in the reference soil varied during the observation time (Fig. 4.2-1). However, the changes were not as clearly seasonal as in the Sb concentrations. In 2013, no seasonal variation could be found. For example in block 1 in 2013, the pH seemed to change almost randomly from the end of May (pH 5.0) to July (5.7) to August (4.3) to September (5.4) and October (5.1). Values of pH in the years 2010, 2011 and 2012 suggested seasonal changes. An example is block 1 in 2012 where the porewater had a pH of 5.3 in June, 4.8 in August, and 5.8 in October. In this year, the other blocks also showed a decrease in pH from June to August. No pH data for October were available.

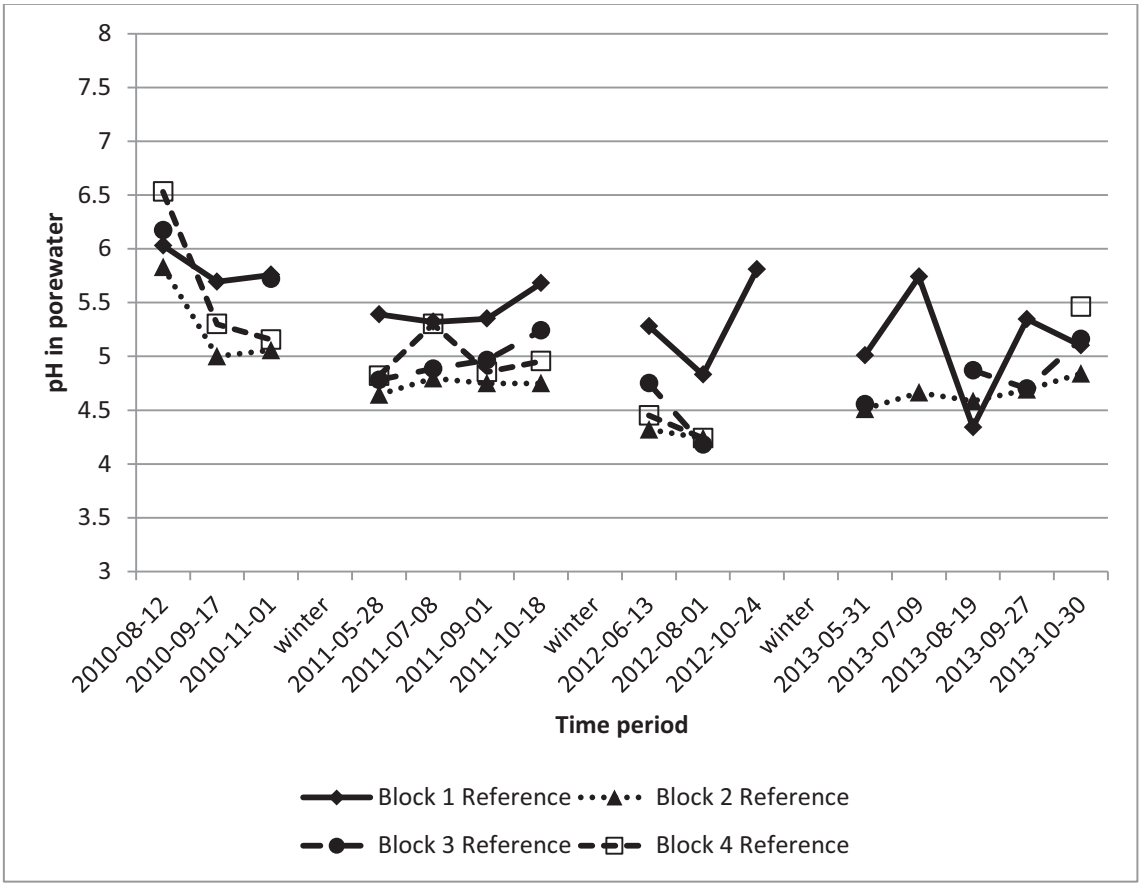

Figure 4.2-1: Average pH in all four reference soils (A sections) from 2010 - 2013.

A correlation between pH, heavy metal and metalloid concentrations was expected. The metal concentrations should increase due to decreased cation sorption at low pH, while the Sb (as the negatively charged oxyanion antimonate) concentration should decrease. This relationship could be seen in a plot with Cu concentration vs. pH (Fig. 4.2-2) in block 1 (2010-2013) (R^2 = 0.636).

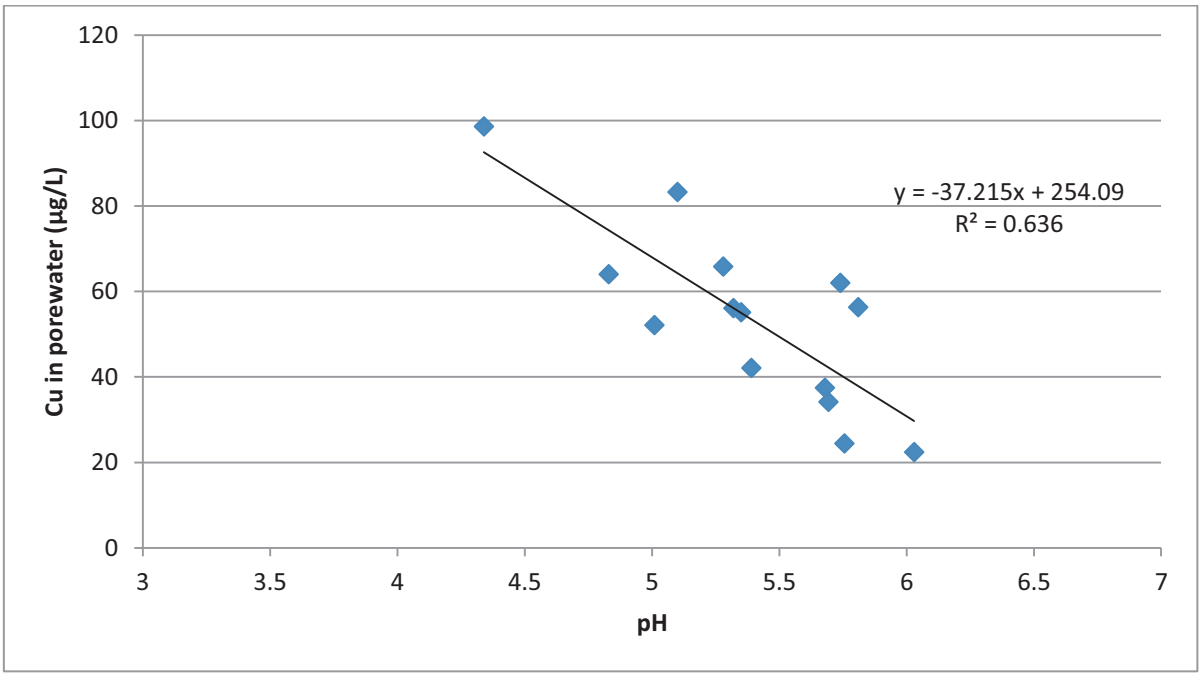

Figure 4.2-2: Correlation of Cu concentration with pH in block 1, section A for the years 2010-2013.

The correlation of Cu concentration and pH in reference porewater in block 1 was an exception and the correlation of the other elements and pH was much weaker (Fig. A.1-1 – A.1-3 in the appendix). In these Figures, the sections from all blocks were included, not only from one as in Figure 4.2-2 above. For the reference soils (all A sections), Cu and Zn had the highest values for R^2: 0.1897 for Cu and 0.2591 for Zn. No correlation was observed between pH and Pb (0.091) as well as pH and Sb (0.0402).

4.3 Element speciation in the untreated soil

Geochemical speciation calculations were done for porewater in the reference soil in blocks 1 and 2 (Fig.4.3-1). A larger percentage of Pb was bound to fulvic acids in block 1 (~79%) than in block 2 (~13%). In block 2, most (~69%) of the Pb occurred as Pb^{2+} whereas this species took only approximately 15% of the share in block 1. Another difference was found in the complexation with bicarbonate. In block 2, $PbHCO_3^+$ took a share of 16% while in block 1 this amounted merely to 2%. Other Pb species were present, but less prominent and thus not labeled in the graphs.

The distribution of species was different among the elements. Lead and Cu occurred to the largest part bound to fulvic acids in block 1. Lead preferred complexation with fulvic acids containing phenolate, while Cu primarily formed complexes with fulvic acids containing carboxylate. Another difference was the total amount of the metal which was bound to fulvic acids (96% of the mobile Cu and 78% of the Pb). In block 2, 46% of the Cu was bound to

DOC, much more than Pb. Zn showed no DOC influence, and occurred largely as Zn^{2+}, Sb as antimonate.

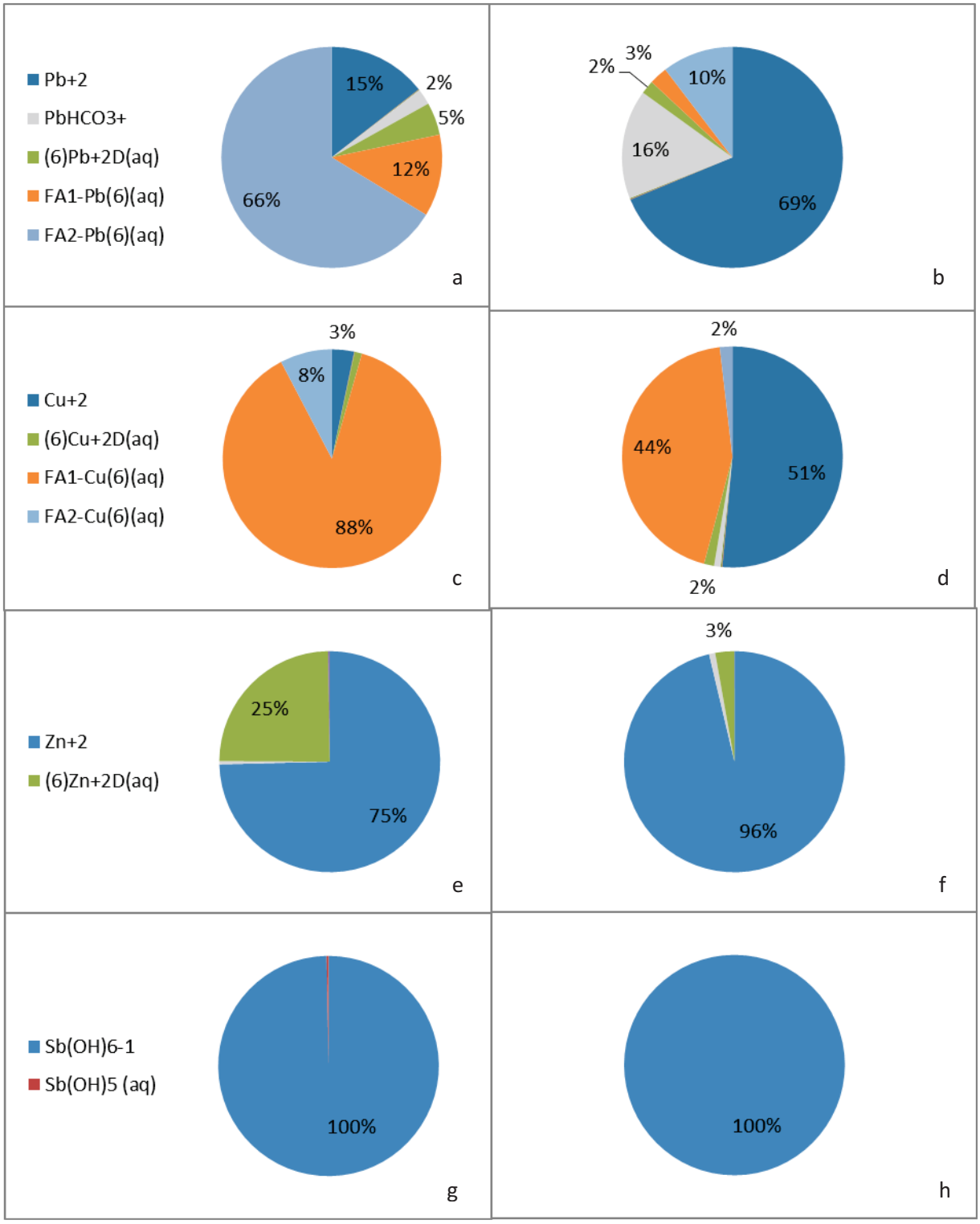

Figure 4.3-1: Speciation in porewater of Pb (a, b), Cu (c, d), Zn (e, f) and Sb (g, h). a, c, e, g: Block 1, section A (reference soil), DOC = 24.8 mg/L, pH = 5.35. b, d, f, h: Block 2, section A (reference soil), DOC = 5.62 mg/L, pH = 4.69. Other species were calculated, but their percentages were very low (< 1%), they are not shown in these charts. FA1 = fulvic acid containing carboxylate; FA2 = fulvic acid containing phenolate anions; (6)Metal+2D = weakly electrostatically bound metal to dissolved fulvic acids. Sampling day: 9/27/2013.

The pH varied slightly among the A sections of blocks 1-3 (5.35, 4.69 and 4.70, respectively). The DOC values differed strongly between block 1 and the other two blocks. With 24.8 mg/l in block 1, it was by far the highest concentration of DOC, while blocks 2 and 3 had values of 5.62 mg/l and 4.91, respectively.

4.4 Porewater concentrations in treated soil and pH

The effects of the soil amendments on sorption are presented in this chapter. The amendments not only provided sorption sites, but also influenced element stabilization by having an impact on porewater pH.

The following four bar diagrams show the Pb concentrations in the porewater on a logarithmic scale. Block 1 and 3 had the same amount of amendments mixed into the soil (2%), block 4 had 4%, and block 2 was used for top application (also 2%).

Figures 4.4-1 and 4.4-3 (blocks 1 and 3) show the results for soils treated the same way and thus show similar Pb sorption. The porewater concentrations of the reference soil (section A) were much higher than they were in the treated sections B and C. This could clearly be seen in the end of September 2013 in block 1, where Pb concentration changed from 1495 µg/L in the untreated reference soil to 6.1 and 6.9 µg/L in the CFH-12&limestone and zerovalent Fe treated soils, respectively. CFH-12&limestone seems to generally have a slightly better sorption capacity than the zerovalent Fe.

Figure 4.4-4 shows that the sorption in soil with 4% amendments mixed in (block 4) is very efficient reaching Pb retention of up to 100%, which is probably influenced by the lower total Pb concentration in the soil in this block (Figure 4.1-2).

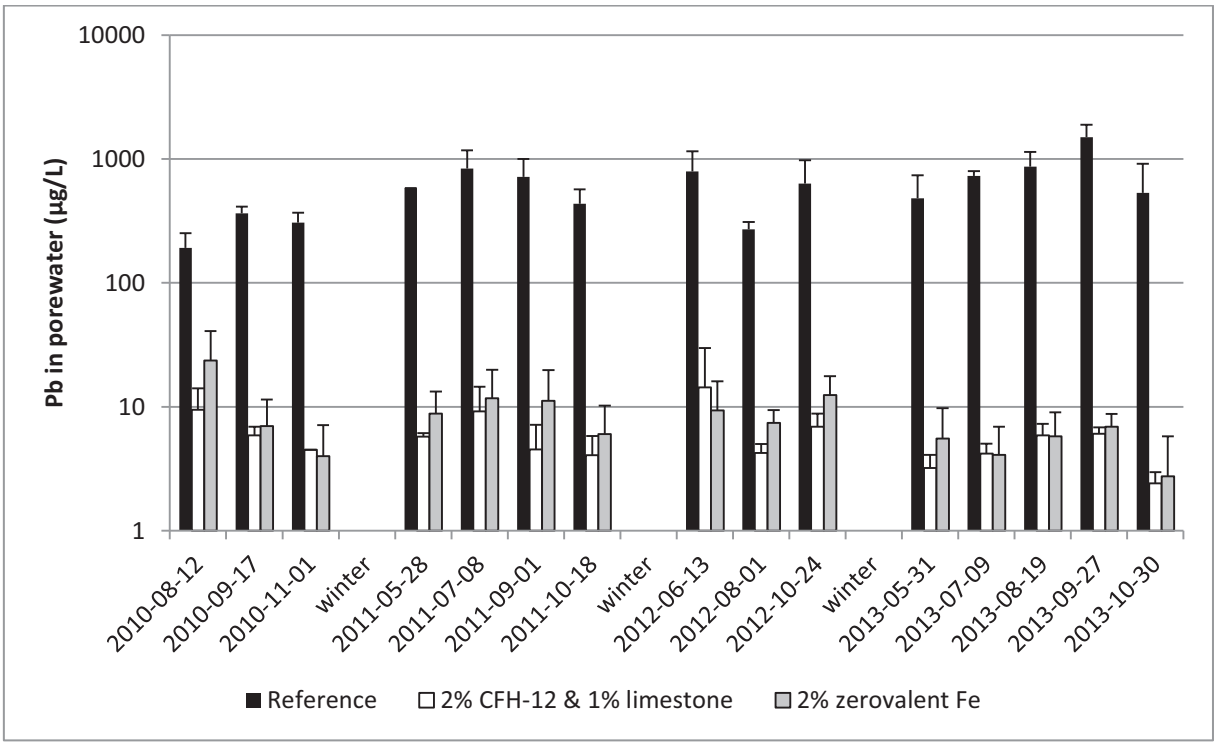

Figure 4.4-1: Average Porewater Pb concentrations in the reference soil, the soil mixed with 2% CFH-12&limestone and the soil mixed with 2% zerovalent Fe in block 1. The error bars show the standard deviation of three replicates (from 2010-2013).

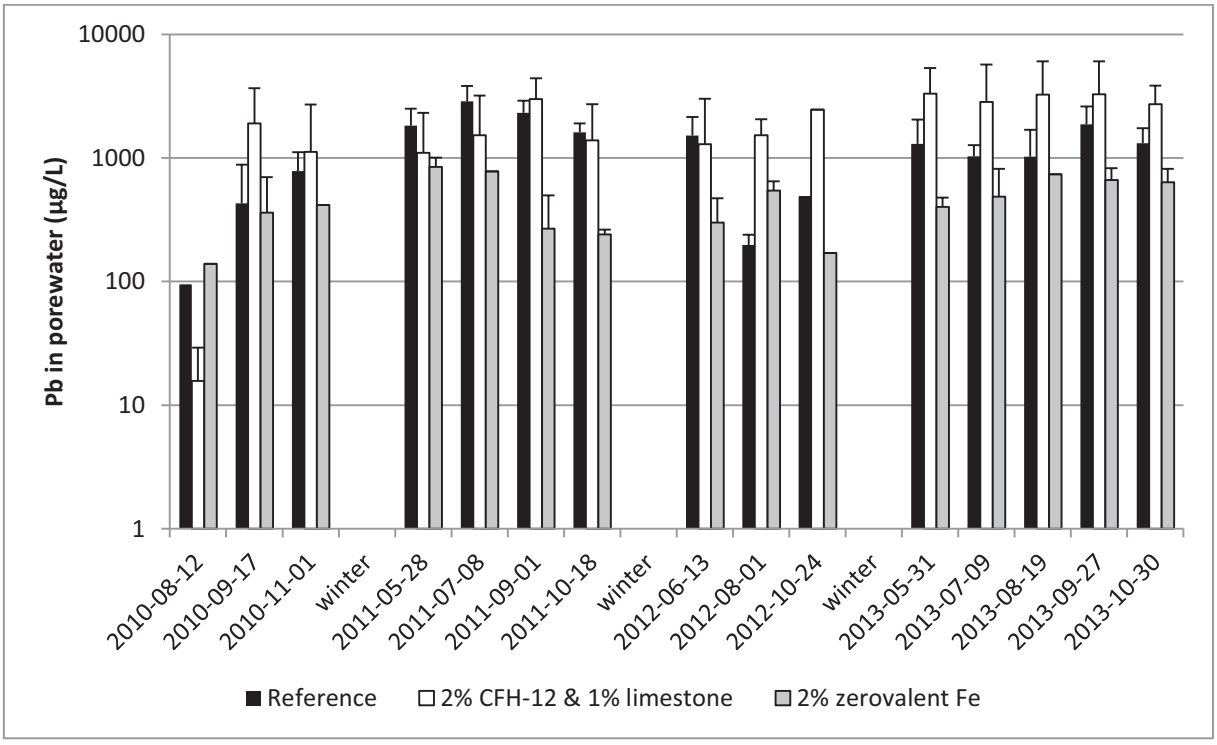

Figure 4.4-2: Average Porewater Pb concentrations in the reference soil and the soils with CFH-12&limestone and zerovalent Fe used in a top application (block 2). The error bars show the standard deviation of three replicates (from 2010-2013).

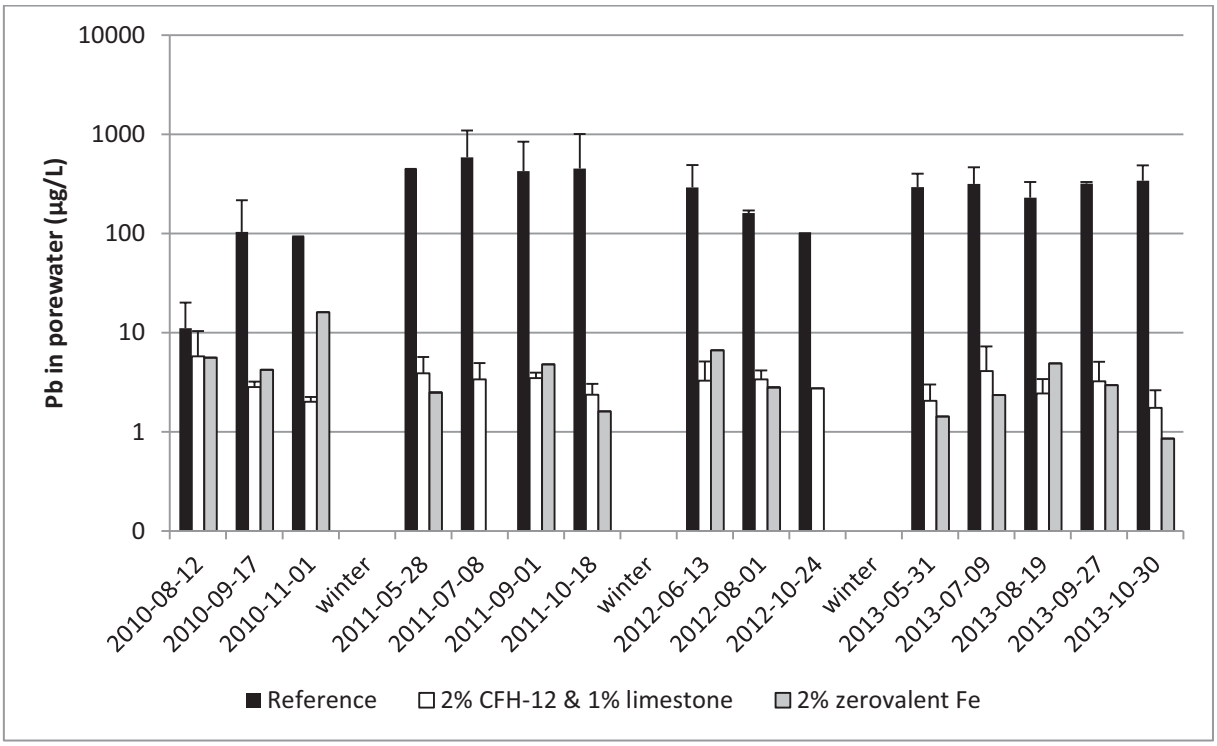

Figure 4.4-3: Average Porewater Pb concentrations in the reference soil, the soil mixed with CFH-12&limestone and the soil mixed with zerovalent Fe in block 3. The error bars show the standard deviation of three replicates (from 2010-2013).

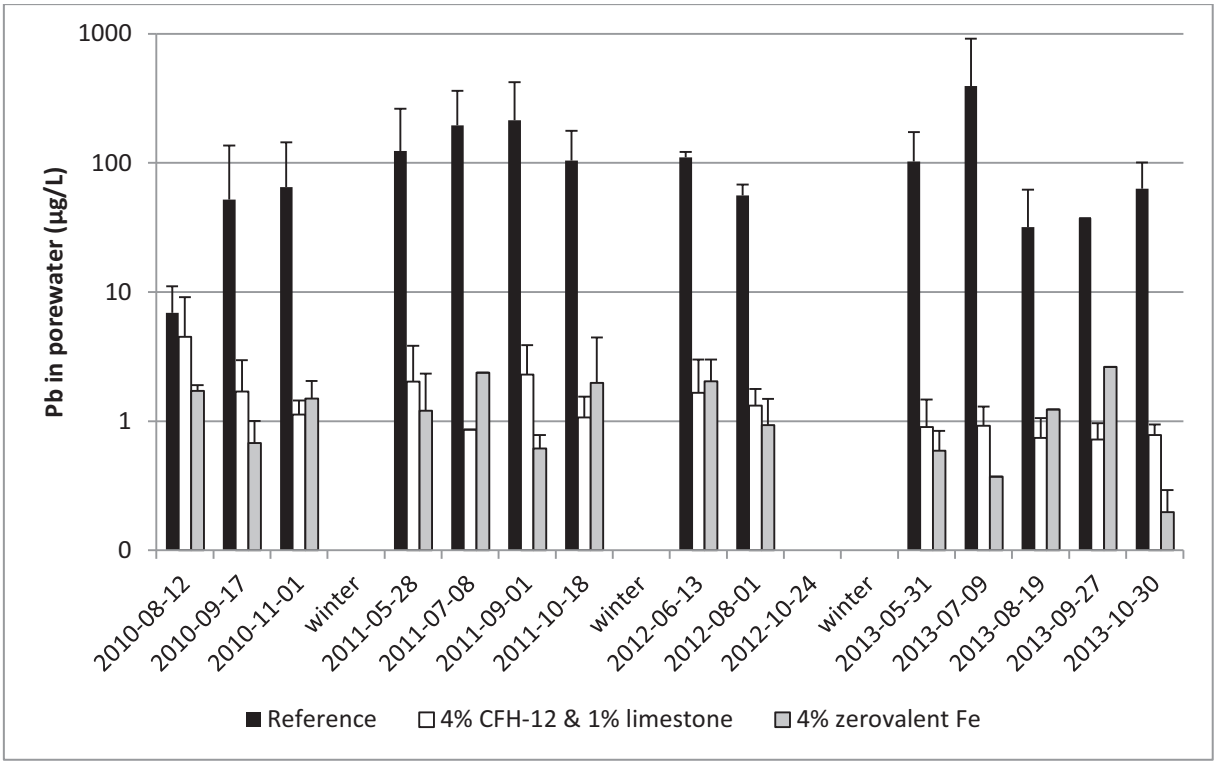

Figure 4.4-4: Average Porewater Pb concentrations in the reference soil, the soil mixed with 4% CFH-12 (+2% limestone) and the soil mixed with 4% zerovalent Fe in block 4. The error bars show the standard deviation of three replicates (from 2010-2013).

Figure 4.4-5 shows Sb concentrations indicating less efficient Sb immobilization by the amendments than for Pb. In block 1 (end of September 2013), concentrations changed from 260µg/L in the untreated soil to 121 and 55µg/L in the CFH-12&limestone and zerovalent Fe treated soils, respectively. This suggests a slightly better sorption of Sb by zerovalent Fe than CFH-12&limestone, possibly due to the increased pH in the soil with added limestone.

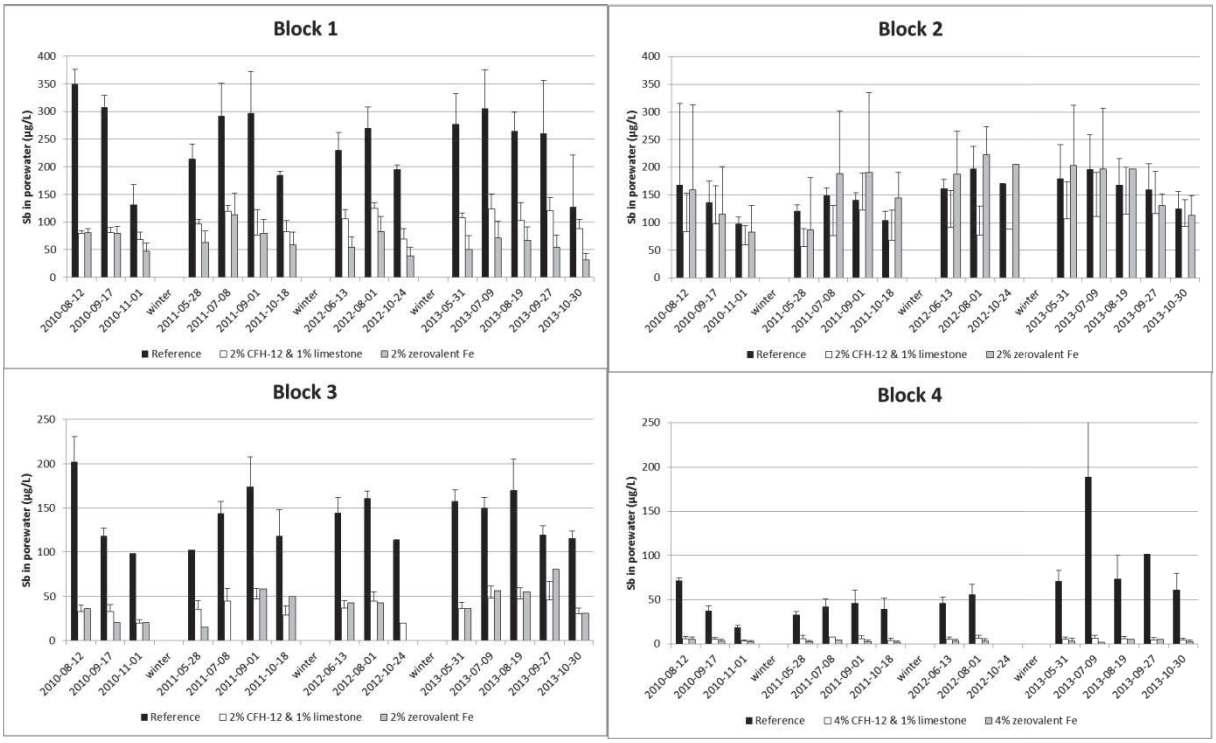

Figure 4.4-5: Average porewater Sb concentrations in block 1-4. The error bars show the standard deviation of three replicates (from 2010-2013).

The amendments used as top applications in block 2 did not seem to have any effect on the sorption of Pb, although concentrations in soil with zerovalent Fe generally had slightly lower values (Figure 4.4-2). However, for CFH-12&limestone treated soil, Pb values increased in comparison to the reference soil, having a negative effect. Sb concentrations in block 2 did not change substantially, but were a little higher in many samples in porewater from zerovalent Fe treated soil and lower in CFH-12&limestone treated soil. Copper and zinc concentrations in block 2 changed in the same way as Pb concentrations (Fig. 4.4-6 and 4.4-7). They increased with the addition of CFH-12&limestone in top-application, and decreased in zerovalen Fe treated soil.

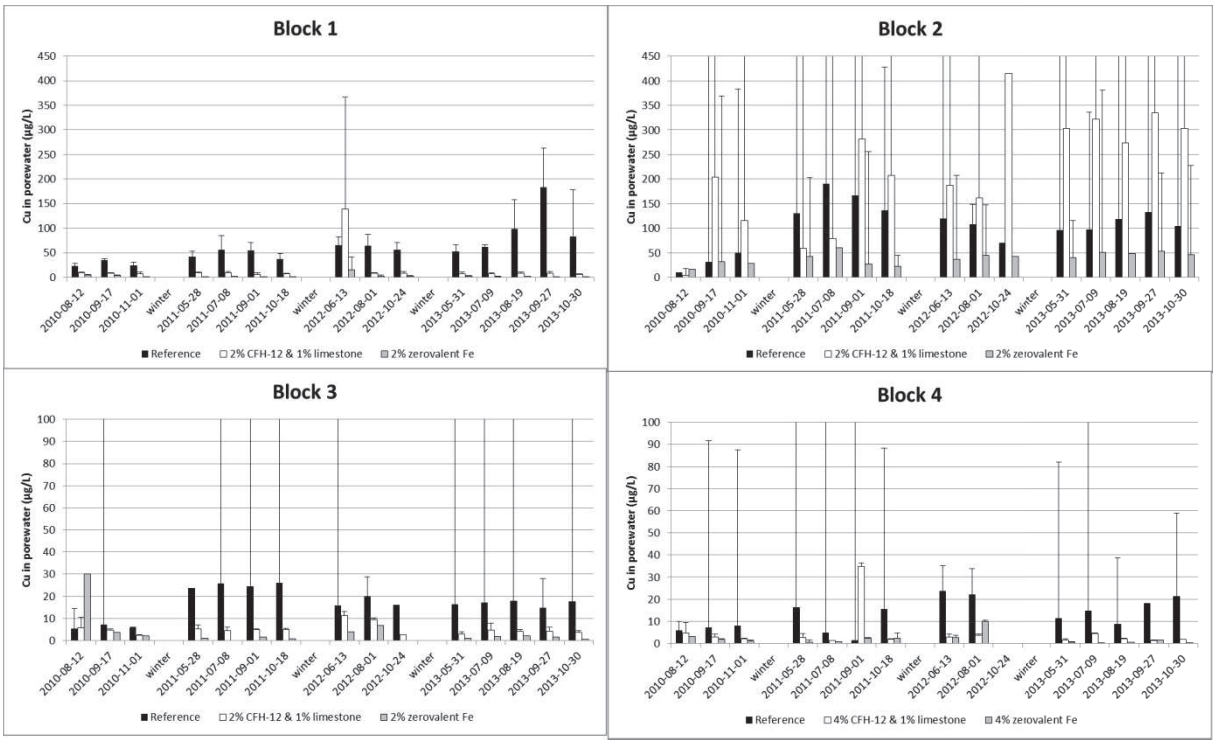

Figure 4.4-6: Average porewater Cu concentrations in blocks 1-4. Note that the maximum concentration on the y-axis in block 1 and 2 go up to 450 µg/L, the ones in blocks 3 and 4 only until 100 µg/L. The error bars show the standard deviation of three replicates (from 2010-2013).

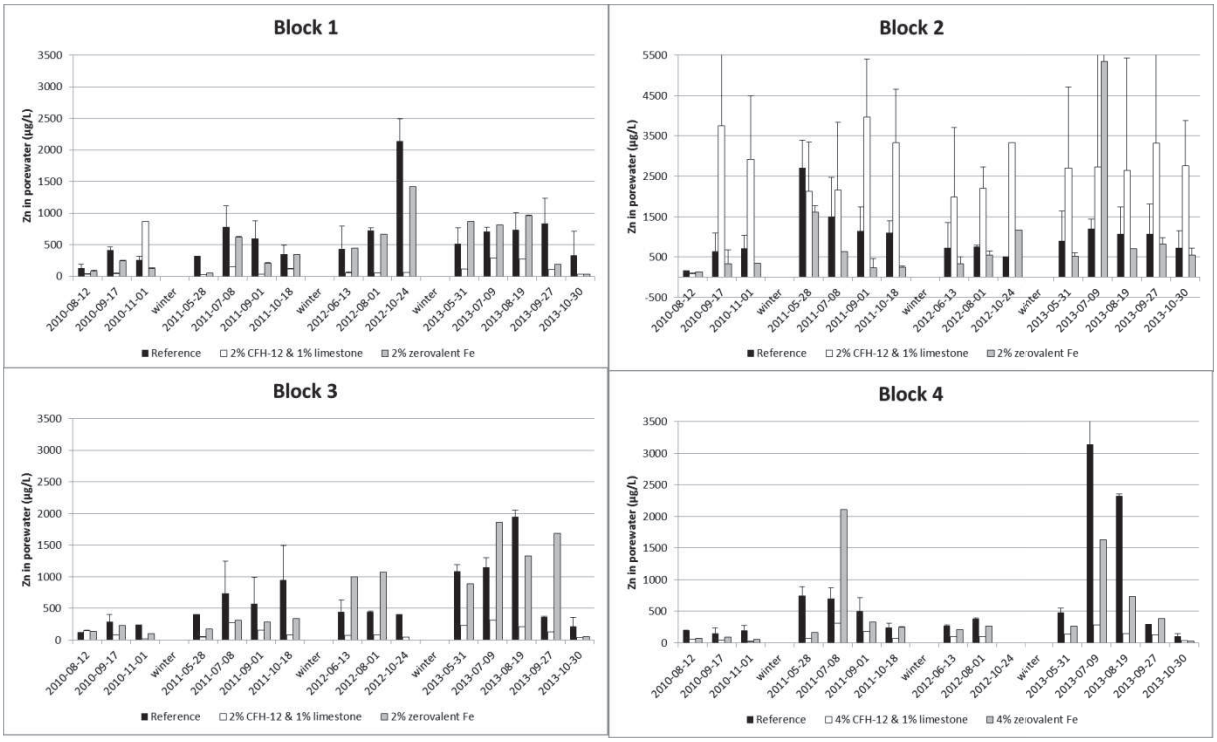

Figure 4.4-7: Average porewater Zn concentrations in blocks 1-4. Note the larger maximum value of 5500 µg/L in block 2 compared to 3500 µg/L in the other blocks. The error bars show the standard deviation of three replicates (from 2010-2013).

In Figure 4.4-8, pH averages in porewater of all four blocks are shown. The pH changed with the addition of amendments into the soil.

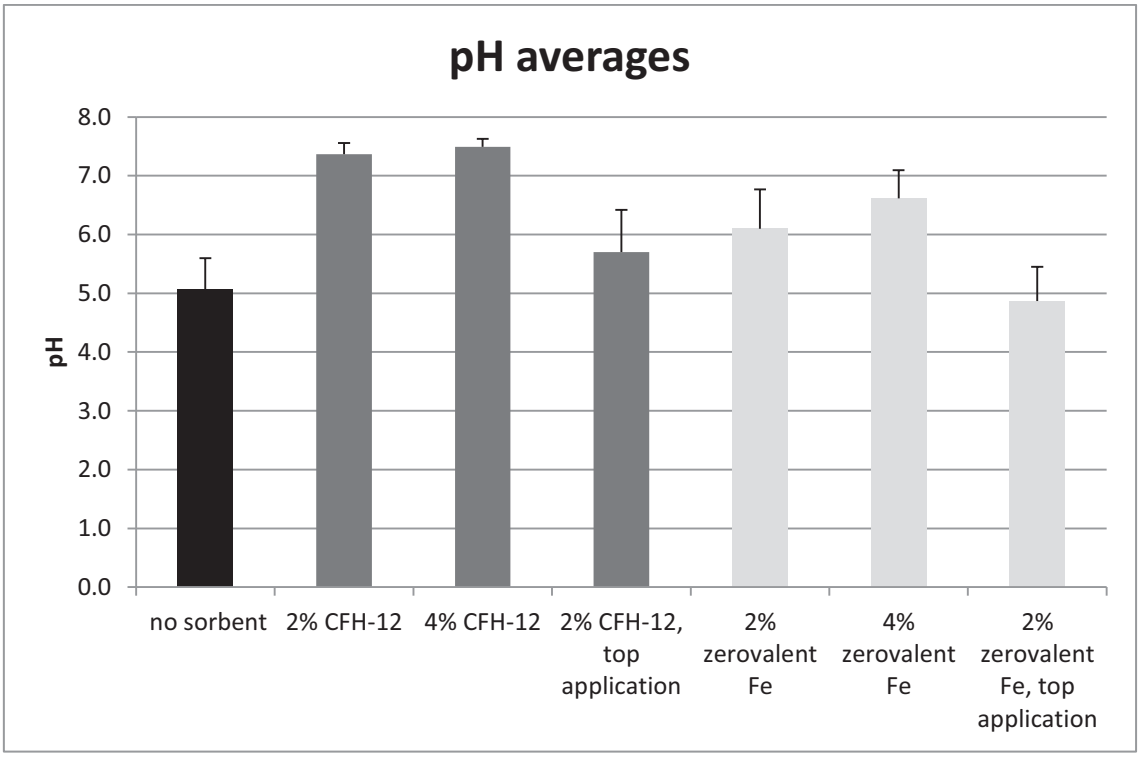

Figure 4.4-8: Average pH values from 2010-2013. The error bars show the standard deviation including all measured values n (from left to right on the x-axis: n = 51, 27, 13, 15, 14, 7, 13).

The average pH was lowest in the reference soils (ph 5). A similar value could be seen in block 2, section C (zerovalent Fe in top application). The highest pH values were found in soil with mixed in CFH-12&limestone. The difference between 2% and 4% CFH-12 amendment was not large, even though the double amount of limestone was added (1% vs. 2%). The porewater pH in the CFH-12&limestone mixed in application was substantially higher compared to the top application. The top application of amendments seemed to have a smaller impact on soil pH than mixing.

As for the reference soil, a correlation between pH and element concentrations was tried for the treated soils (Fig. A.1-1 – A.1-3). Generally, the B sections (CFH-12&limestone amended soils) showed the lowest correlation between pH and Cu, Zn, Pb and Sb. The coefficient of determination R^2 ranged between 0.0045 (Zn) and 0.0817 (Pb). Except for Cu, the C sections showed higher values for R^2, with Zn being the highest: 0.4407 (Zn) (0.2118 (Pb), 0.2148 (Sb). Block 2 was excluded from the correlation, because of the differing amendment application.

Taking a closer look at the B sections, it is interesting to notice the variability in element concentration in a relatively narrow range from pH 7 to 8 (see Figure A.1-2 in the appendix).

4.5 Element speciation in treated soil

Using the computer program Visual MINTEQ, the speciation was calculated for Cu, Zn, Pb and Sb. To show those results, one sampling day was chosen (27th September 2013) as an example.

The speciation of Pb in porewater varied depending on the used amendment in the soil (Fig. 4.5-1). The comparison of the results of porewater from soil amended with CFH-12&limestone and zerovalent Fe showed a main difference in the distribution of Pb between the two types of fulvic acid defined by the model. No free Pb^{2+} occurred in the water. In soil mixed with CFH-12&limestone (section B), approximately 99% of Pb was bound to fulvic acids containing phenolate (FA2), and only approximately 1% to fulvic acids containing carboxylate (FA1) (Fig. 4.5-2 a). The Pb speciation for soil with zerovalent Fe looked very similar. Most of the Pb was bound to FA2 (~87%) and FA1 (~12%) (Fig. 4.5-1 b).

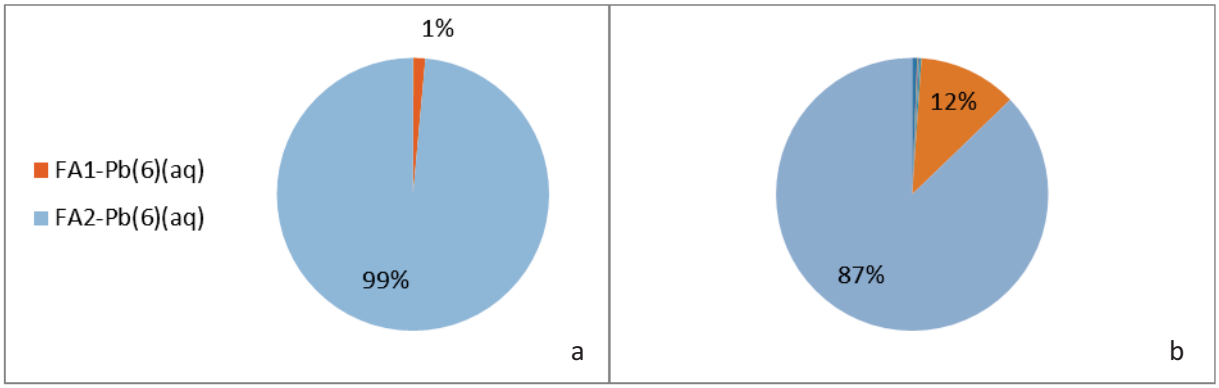

Figure 4.5-1: Pb speciation. a: block 1, section B (CFH-12&limestone), pH = 7.51. b: block 1, section C (zerovalent Fe), pH = 6.45. Other species were calculated, but their percentages were very low (< 1%), and they are not shown in these charts. FA1 = fulvic acid containing carboxylate; FA2 = fulvic acid containing phenolate anions. Sampling day: 9/27/2013.

Cu was bound to ~100% to fulvic acids in CFH-12&limestone amended soil (Fig.4.5-2), but 97% of that was FA2-Cu(6), not FA1-Cu(6) as in the untreated soil of the same block (Fig. 4.3-1). In zerovalent Fe treated soil, Cu occurred in both fulvic acids to ~50%. The speciation of Zn did not change significantly by adding sorbents, staying as Zn^{2+} in the solution.

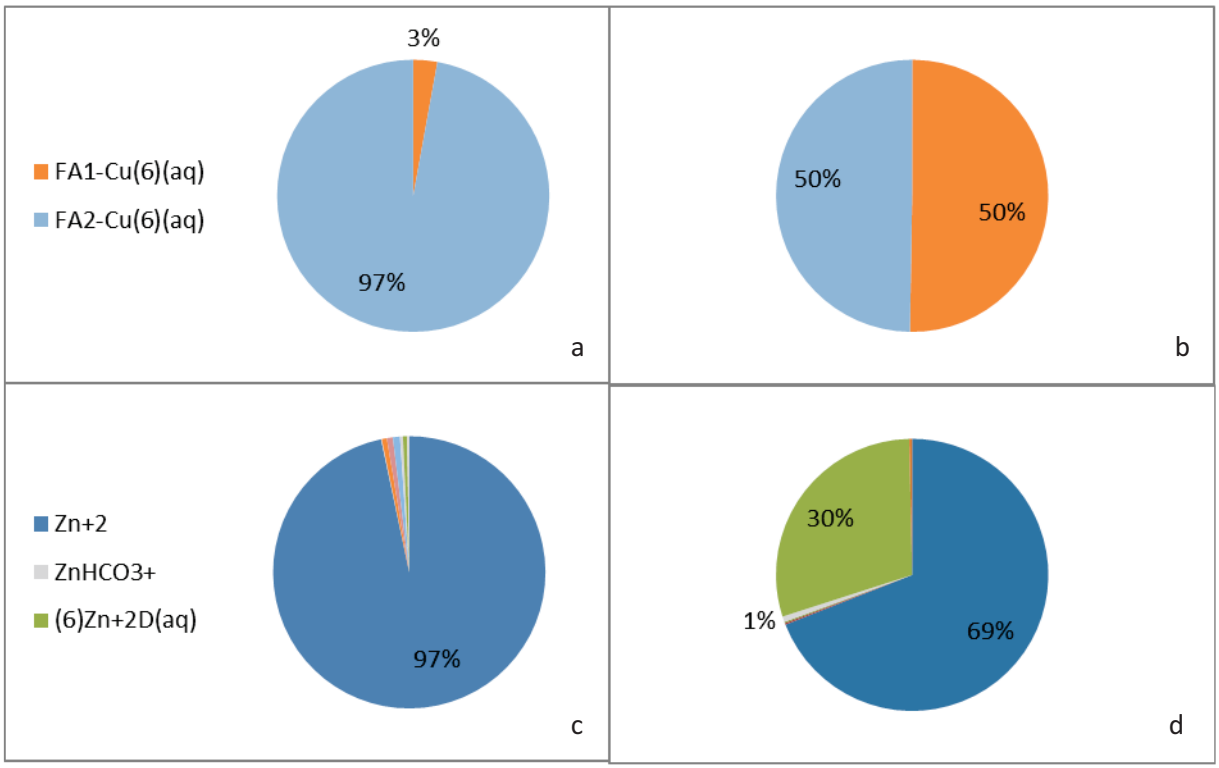

Figure 4.5-2: Cu (a, b) and Zn (c, d) speciation. a, c: Block 1, section B (CFH-12&limestone), pH = 7.51. b: Block 1, section C (zerovalent Fe), pH = 6.45. Other species were calculated, but their percentages were very low (< 1%), and are not shown in these charts. FA1 = fulvic acid containing carboxylate; FA2 = fulvic acid containing phenolate anions. Sampling day: 9/27/2013.

The speciation of Sb did not show much variety. In the porewater of the reference soil, Sb occurred primarily as antimonate ($Sb(OH)_6^-$) with a percentage of ~99.7%. The rest was $Sb(OH)_5$ in solution. When amendments are added, the latter species is basically eliminated (Fig.4.5-3).

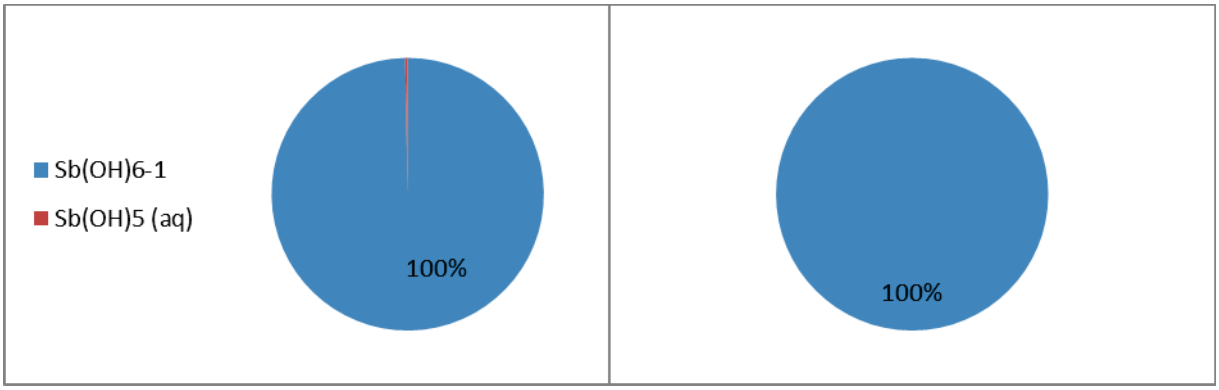

Figure 4.5-3: Sb speciation. a: block 1, section A (reference soil), DOC = 24.8 mg/L, pH = 5.35. b: block 1, section B (CFH-12&limestone treated soil), pH = 7.51. Sampling day: 9/27/2013.

Top application

When comparing the speciation of Pb in porewater among treated soils in block 2 (top application), the differences were small (Fig. 4.5-4). Significant was the amount of Pb bound to fulvic acids. The amount of Pb bound to DOC was ~31% in section B, thus much higher than in section C (~7%). Differences in DOC concentration (13.5 mg/L in section B, 5.3 mg/L in section C) and pH (pH 5.45 in section B, pH 3.98 in section C) may explain this.

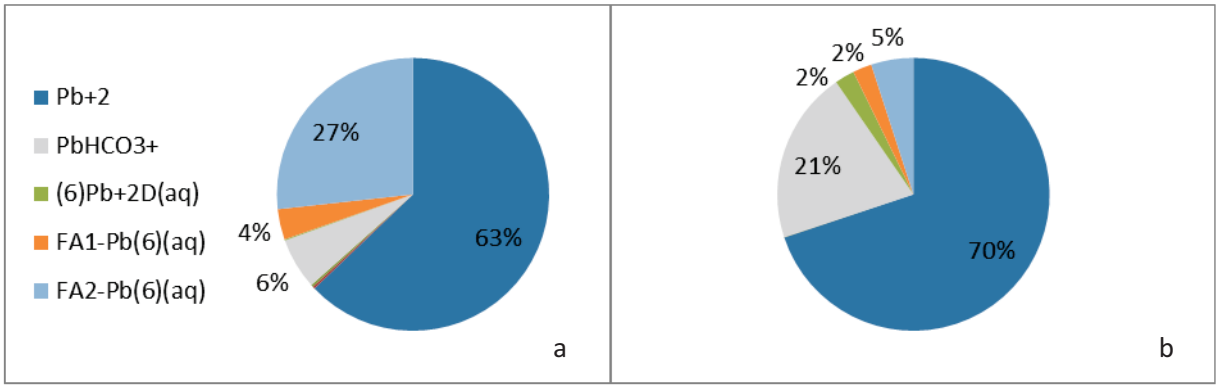

Figure 4.5-5: Pb speciation. a: block 2, section B (top application of CFH-12&limestone), pH = 5.45. b: block 2, section C (top application of zerovalent Fe), pH = 3.98. Other species were calculated, but their percentages were very low (< 1%), and are not shown in these charts. FA1 = fulvic acid containing carboxylate; FA2 = fulvic acid containing phenolate anions; (6)Metal+2D = weakly electrostatically bound metal to dissolved fulvic acids. Sampling day: 9/27/2013.

4.6 X-ray diffraction

An XRD analysis of the soil was carried out for determining the presence of iron minerals, carbonates and (hydr)oxides containing Pb, Cu, Zn or Sb. A study on soil from the same shooting range has been carried out by Herzel (2012)[30]. He collected iron minerals with a magnet and by color for an XRD analysis. Birnessite (manganese-oxide), rutile (titanium-oxide), lepidocrocite, goethite (Fe-hydroxides) and magnetite could be identified. The copper (hydr)oxides malachite covering bullet surfaces and cuprite around cracks in the bullet mantle were detected by Raman spectroscopy. Anglesite and cerussite were present where the bullet was in direct contact with the soil.[30]

In this study, the Cu, Pb and most of the Fe minerals were not detected. The XRD patterns of the highest peaks correspond to the typical soil minerals quartz (SiO_2), albite ($NaAlSi_3O_8$) and microcline ($KAlSi_3O_8$) (Fig. 4.6-1, 4.6-2 and 4.6-3). The sheet silicate clinochlore ($(Mg, Fe^{2+})_5Al(Si_3Al)O_{10}OH_8$) had small peaks throughout the whole investigated range from 10 - 60° 2theta (see fig 4.6-2 at 12.5° and 18.8° 2 theta).

The XRD analysis of soil samples from blocks 1 and 2 showed no substantial differences between all six analyzed sections (Fig 4.6-1). Notable was an intensity peak at ~29.5° 2theta for samples taken from the B sections. Block 1, section B was mixed with CFH-12&limestone, and in block 2, section B, the same amount and type of amendment was added in a top-application. The peak was identified as calcite (Fig. 4.6-2).

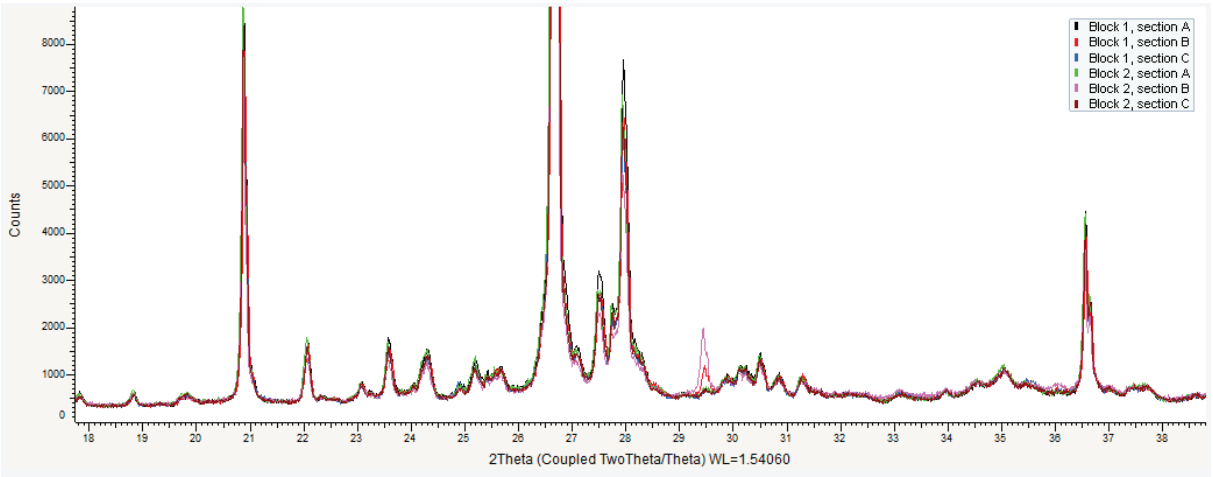

Figure 4.6-1: The Figure depicts the results of the XRD analysis of all six samples (block 1, sections A, B, C and block 2, sections A, B, C) joined into one plot from ~18° - ~39° 2theta. There are only minor differences between the sections. Notable are the two B sections with a higher peak at a ~29.5° 2theta. This peak was identified as calcite.

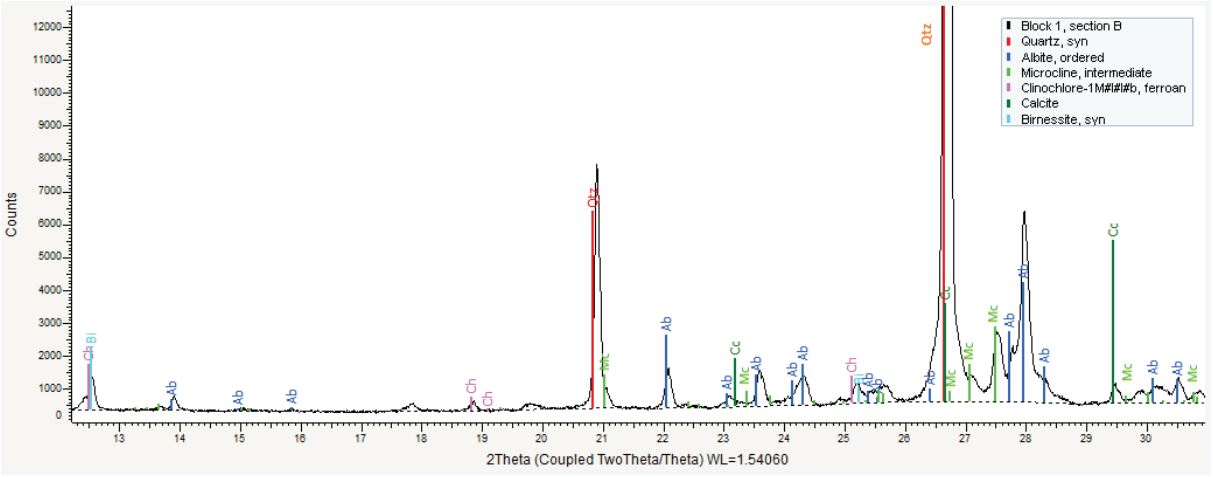

Figure 4.6-2: The XRD analysis shows a distinct calcite (Cc) peak at ~29.5° 2 theta, and well pronounced birnessite (Bi) peaks at 12.5° and 25.2° 2theta. Qtz = Quartz, Ab = Albite, Mc = Microcline, Ch = Clinochlore.

Peaks for birnessite, a manganese oxide, were also recognized. The search for iron minerals proved difficult. In soil treated with Fe-based amendments, hematite and magnetite may be expected, but were not detected. Goethite, with distinct peaks at 17.8° and 33.1° 2theta in Figure 4.6-3, was probably present. Other peaks for a Fe-hydroxide called akaganeite

(FeO(OH, Cl)) are shown in the same Figure, but the possibility for its existence is low, because the best fitting peak for this coincides with the one for quartz at 26.8° 2theta.

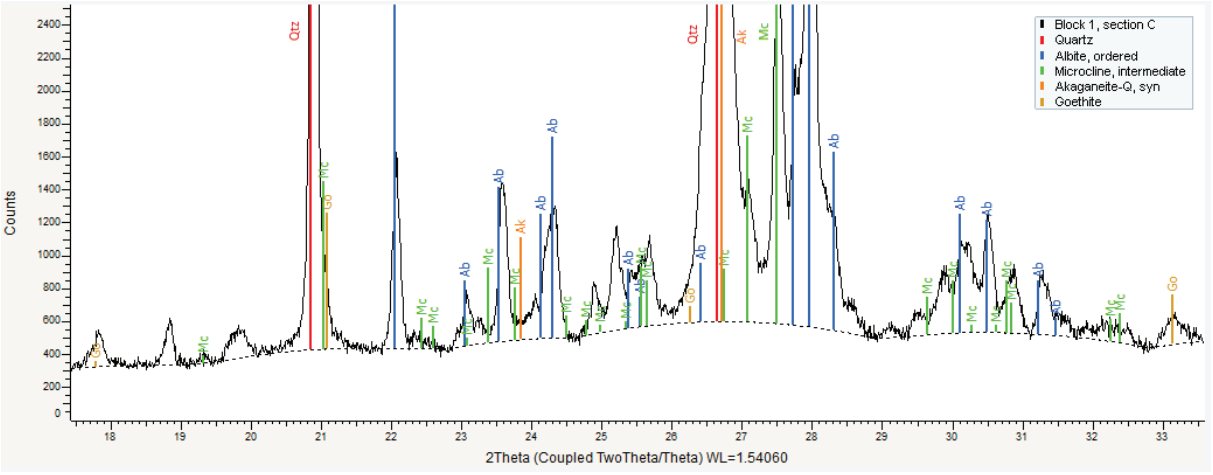

Figure 4.6-3: XRD pattern for soil in block 1, section C: The goethite (Go) peaks at 17.8° and 33.1° 2theta are distinct. The very high akaganeite (Ak) peak at 26.8° 2theta is possibly not relevant due to the overlying quartz (Qtz) peak. Ab = Albite, Mc = Microcline.

4.7 Surface water

Surface water concentrations were lower than porewater concentrations from the stop butt soil, but Pb and Sb values were much higher than normal background values (Table 5.1-1), ranging from ~100-840 µg/L for Pb and ~42-280 µg/L for Sb (Table B.1-6 and Fig. 4.7-1).

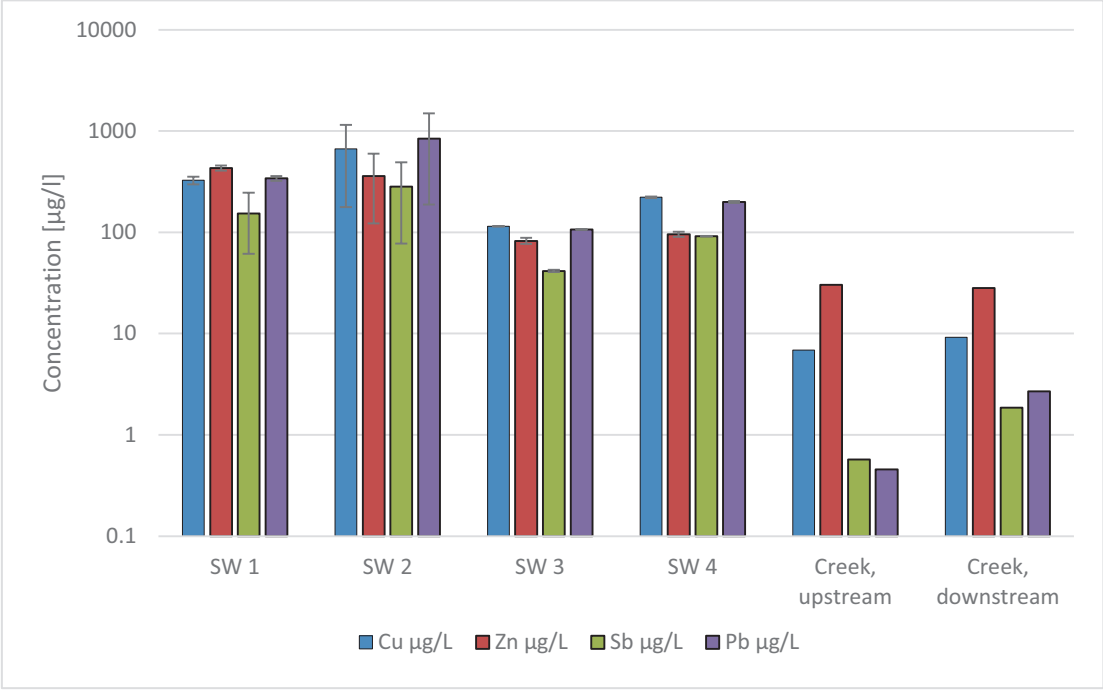

Figure 4.7-1: Surface water concentrations.

When comparing the data for samples taken from the creek upstream with the ones taken from downstream, there were no differences in Cu and Zn concentrations. However, Pb and Sb concentrations increased from 0.5-2.7µg Pb/L and ~0.6-2 µg Sb/L.

5. Discussion

5.1 Soil without sorbents

Investigating the effects of chemical stabilization of contaminants in soil requires knowledge about the contamination when left untreated. This is also critical for choosing the correct type of amendment and type of application. In order to achieve this with a long-term goal, it is important to take a look at the time it would take for the contaminants to be carried out of the soil if the shooting range at Steinsjøen were left untreated. An estimate is made at the end of this chapter.

Contamination levels

Lead and antimony concentrations in porewater from the untreated bullet trap soil generally exceeded the EU (European Union) drinking water limits, Norwegian environmental quality standards (EQS) and typical background concentrations (Table 5.1-1). From 2010 to 2013, Pb levels ranged from 7-2870 µg/L. The upper limit for drinking water was set at 10 µg Pb/L by the EU council directive on the quality of water intended for human consumption. Antimony concentrations (19-349 µg/L) were above the EU limit of 5 µg/L in each reference section. The concentration of Cu (2-191µg/L) laid within the EU limits of 2000µg/L.

Concentrations in surface water collected in front of the stop butt zone were also significantly higher than EU limits (up to 80 times for Pb) and EQS (Table 5.1-1). The EQS values depicted in the table represent condition IV (of V) which is classified as "strongly contaminated" in the 1997 SFT (statens forurensingstilsyn) report[31]. Water from the creek downstream of the shooting range indicated very strong contamination of Pb and Cu in regards to this classification. No values for Sb are given in the report.

	Pb (µg/L)	Sb (µg/L)	Cu (µg/L)	Zn (µg/L)
Steinsjøen porewater (Tables B.1-1 to B.1-5)	7 - 2870	19 - 349	2 - 191	113 - 2710
Steinsjøen surface water (Table B.1-6)	107 – 841	42 - 284	115 – 665	82 - 431
Steinsjøen creek downstream (Table B.1-6)	3	2	9	28
EU limit[32]	10	5	2000	-
EQS[31]	2.5 - 5	-	3 - 6	50 - 100
Background concentrations[33, 34]	< 1	0.05 - 0.1	-	-

Table 5.1-1: Lead, Sb and Cu concentrations in the porewater of untreated Steinsjøen bullet trap soil, surface water, creek water draining the area, the EU drinking water limits, EQS (Norwegian environmental quality standards) values for strongly contaminated water (condition IV, where I is not and V is heavily contaminated) and typical background concentrations.

Element speciation in porewater

In untreated soil, the speciation of Pb in the reference soil (section A) showed differences in blocks 1 and 2 (see Fig. 4.3-1). Much more of the Pb was bound to fulvic acids in samples from block 1 (~78%) than from block 2 (~13%). This could be explained by the higher pH of 5.35 in block 1, compared to pH 4.69 in block 2. A higher pH (fewer protons in solution) leads to a larger proportion of Pb bound to DOC. At pH 7, nearly 100% of all Pb is usually bound to DOC (see also chapter 2.1 Element properties). Another factor is the total DOC content in the porewater, which was approximately five times higher in block 1 (~25 mg/L) than in block 2 (5.6 mg/L). The Pb reference concentrations were similar with 1495 µg/L in block 1 and 1874 µg/L in block 2 (Fig. 4.4-1 and 4.4-2), and therefore were probably not the deciding factor. The porewaters in the reference soils of block 2 and 3 had similar values for pH, DOC, and thus showed a similar distribution of Pb species. The data from the porewater in block 3 therefore confirmed a dependence on pH and DOC regarding speciation.

Copper and lead behaved opposite in respect to the type of DOC. Complexation may depend on preference of one ion over the other by the different fulvic acids. According to the geochemical modeling, Cu preferred complexation with fulvic acids containing carboxylate anions (FA1-Cu(6)), Pb with phenolate anions (FA2-Pb(6)). The pH also plays a role. The lower the pH, the fewer complexes are formed by cationic heavy metals with DOC due to competition with H^+ ions. Zinc occurred primarily as Zn^{2+}, and had nearly no interaction with DOC in the reference soil. This did not change with increased pH values in the soil influenced by limestone in block 1. Nearly all Zn is expected to be in complexation with DOC at pH levels >6.5 (see chapter 2.1.). As this was not showing in the results, it is possible that a DOC preference for Cu, Pb or other cations exists.

Antimony occurred primarily as pentavalent Sb (Sb(V)) in antimonate ($Sb(OH)_6^-$). Only small amounts of $Sb(OH)_5$ were calculated by Visual MINTEQ. There was no sign of any Sb(III) species in the porewater solution which is in accordance with Mitsunobu et al. (2005)[35] and Johnson et al. (2005)[8].

Seasonal variation of porewater contaminant concentration

Monitoring the porewater of the untreated bullet trap soil showed that the concentration of contaminants varied seasonally (see Fig. 4.1-1 – 4.1.4). Possible reasons for naturally occurring variations in Cu, Zn, Pb and Sb concentrations are related to pH, DOC content, the weathering rate and the amount of water input.

The sorbing capacity of minerals and compounds increases for metals occurring as cations with increasing pH, therefore a positive correlation between concentrations and pH is expected. A tendency for this could be seen for Cu within one section (A of block 1, see Fig. 4.2-2), but has proven difficult for other elements and Cu when combining pH values and Cu concentrations of all relevant sections (see Fig. A.1-1 – A.1-3). This is probably because of other factors influencing sorption. For example, a higher DOC content in the porewater may lead to increased solubility due to complexation.

Another possible explanation for higher element concentrations in the summer months is the weathering rate which is dependent on the temperature (in addition to pH). Variations may also occur through differences in the amount of water infiltration. In periods with a larger water input, the porewater gets diluted. This may happen in periods with higher precipitation or during the snow melt. Although porewater concentrations varied from year to year (7-782 µg/L in 2010 and 104-2870 µg/L in 2011 for Pb; see Fig. 4.1-2), there was no general increase or decrease, which is an indication for a relatively constant weathering rate. This is an important note when analyzing the data from amended soil. It needs to be considered for evaluating the sorption efficiency.

Estimate of long-term leaching from untreated soil

The following calculation shows how much time it may take to leach out the total metal and metalloid amount from the shooting range soil. The calculation is shown for Sb here as an example. The amount of soil in one section (A, B, C) is approximately 1.5 m^3.[28] The average precipitation in the area is approximately 1000 mm/year[3], and ~50% is assumed to infiltrate the soil (500 mm/y = 0.5 m^3/y). The Sb concentration in the reference soil porewater ranges between 20 and 350 µg/L. The average Sb concentration in the porewater of the reference soils of all four blocks is ~150 µg/L (Table B.1-5). Thus the total Sb amount leaching out of the soil is: 0.15 g/m^3 x 0.5 m^3/y = 0.075 gram per year. The total concentration of Sb in soil (block 1) is 123 mg Sb/kg_{soil} = 123 g/t_{soil} (Table 5.1-2). The known variables are:

Volume of the soil:	$V_{total} = 1.5m^3$
Estimated density of the soil:[28]	$\delta_{soil} = 1.8kg/L = 1.8t/m^3$
Mass of the soil in one section:	$M_{soil} = 1.8t/m^3 \times 1.5m^3 = 2.7t$
Mass of total Sb in one section:	$M_{total\ Sb} = 2.7t \times 123g/t = 332g$
Dissolved Sb leaching per year:	$Q_{Sb\ total} = 0.075g/y$

Based on these variables, the time it takes for all the Sb in the soil to leach out with the porewater can be calculated:

$$t = \frac{332g}{0.075g/y} = \sim 4427y$$

Calculated in the same way, the leaching time for Pb with a total concentraion of 1112 mg/kg and Cu with 88 mg/kg (Table 5.1-2), is ~10500y and ~9500y, respectively (average concentration of reference soil outflow is 570 µg/L (Pb) and 50 µg/L (Cu)). According to this very theoretical model, it would take almost 10000 years to leach out all of the lead. Therefore, it is very important to find long-term stabilization methods.

	Block 1	Block 2	Block 3	Block 4
pH (average)	4.3-6.0	4.2-5.8	4.2-6.2	4.2-6.5
TOC %	0.41	0.42	0.52	-
Cu mg/kg	88 +/-4	61 +/-22	41 +/-4	46
Pb mg/kg	1112 +/-125	486 +/-200	356 +/-109	14055
Sb mg/kg	123 +/-21	54 +/-23	40 +/-14	671

Table 5.1-2: Porewater pH, soil total organic carbon (TOC), Cu, Sb and Pb soil concentrations[33].

5.2 Effect of soil amendments

In general, the retention efficiency was very good for both amendment types in the mixed in applications. Below is a table (5.2-1) showing Pb, Sb, Cu and Zn concentrations in porewater of untreated and treated soil, EU drinking water limits and Norwegian environmental quality standards (EQS). It shows a substantial Pb concentration decrease in both amendment types to values close to both the EU drinking water limit and EQS. Antimony concentrations were substantially lower, but still too high (15-123 µg/L) considering these limits. Zn had a very large range from below the limits to concentrations far above them.

	Pb (µg/L)	Sb (µg/L)	Cu (µg/L)	Zn (µg/L)
Reference soil (Tables B.1-1 to B.1-5)	7 - 2870	19 - 349	2 - 191	113 - 2710
2% CFH-12&limestone (Tables B.1-1 to B.1-5)	2 - 14	19 – 123	2 – 139	17 – 870
2% zerovalent Fe (Table B.1-6)	1 – 24	15 – 113	1 – 30	36 - 1857
EU limit[32]	10	5	2000	-
EQS[31]	2.5 - 5	-	3 - 6	50 - 100
Background concentrations[33, 34]	< 1	0.05 - 0.1	-	-

Table 5.2-1: Lead, Sb and Cu concentrations in the porewater of treated (2% amendment) Steinsjøen bullet trap soil, the EU drinking water limits, EQS (environmental quality standards Norway) values for strongly contaminated water (condition IV, where I is not and V is heavily contaminated) and typical background concentrations.

Average retention was calculated using these data. Pb retention in blocks 1, 3 and 4 is above 94% (Fig. 5.2-1). Major differences in Pb retention efficiency between soils mixed with 2% and 4% amendment were not observed. All values were at or above 94%.

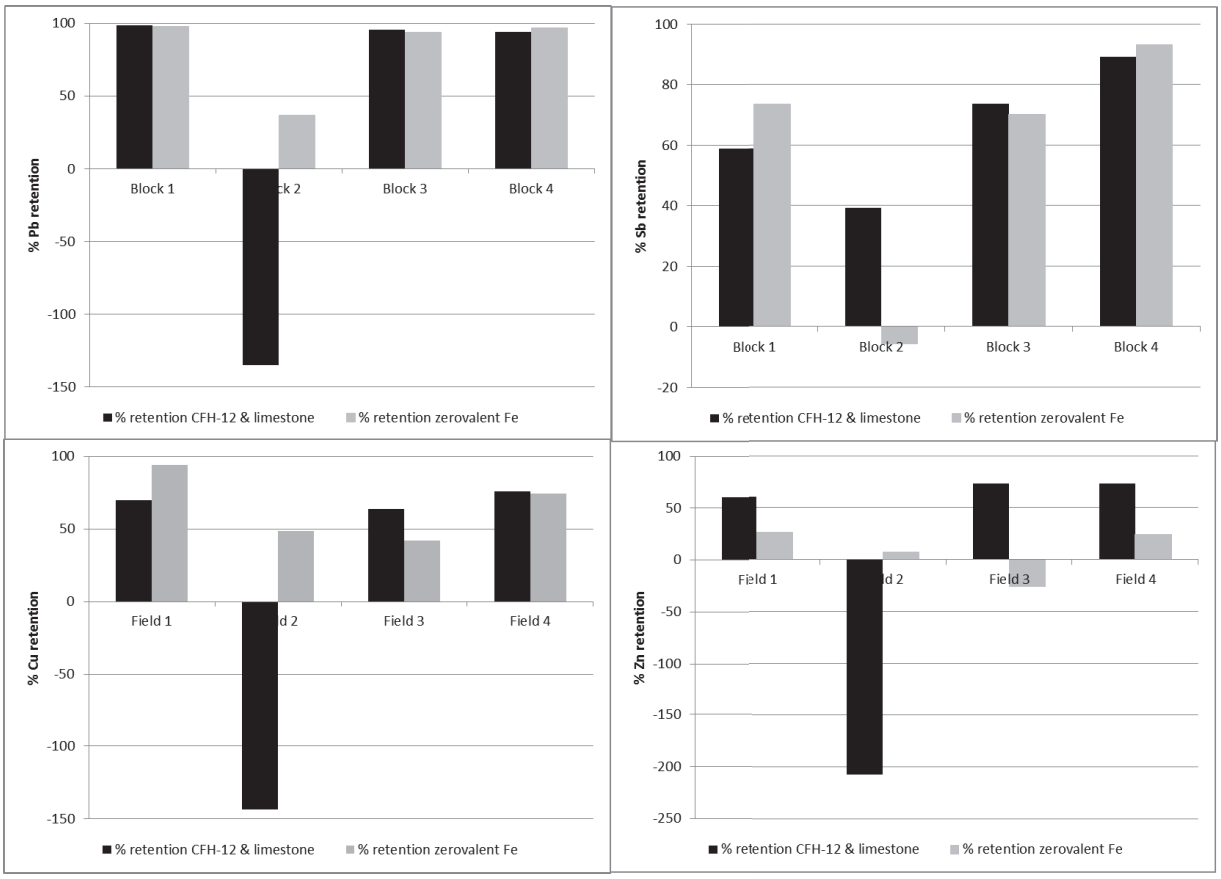

Figure 5.2-1: Average Pb, Sb (top), Cu and Zn (bottom) retention 2010-2013.

For Sb, the retention was overall less (59% - 93%) compared to Pb (Fig. 5.2-1). For both amendment types, only slightly better sorption was achieved with higher sorbent concentrations (4%). In the soils with 2% sorbent mixed in, the highest Sb retention was

gained in CFH-12&limestone treated soil in block 3 (74%). The negatively charged oxyanion was sorbed less efficiently at high pH values, because of an increased amount of negatively charged mineral surfaces. However, the higher pH in the porewater of the soil treated with CFH-12&limestone did not lead to reduced sorption of Sb. The sorption of Sb was similarly high in zerovalent Fe treated soil in block 1 (73%). Very good Sb retention with a maximum of 93% was found in block 4 with 4% zerovalent Fe. The soil amended with 4% CFH-12&limestone also showed very good Sb retention, probably influenced generally by lower Sb concentrations in this block (Fig. B.1-5).

Copper and zinc retention was in general lower compared to Pb retention. For 2% CFH-12&limestone mixed into the soil, the average values were 64% (block 1) and 70% (block 3) for Cu, and 60% and 73% for Zn (Fig. 5.2-1). In zerovalent Fe treated soil, a difference between Cu and Zn retention could be seen. Copper retention averages were 94% (block 1) and 42% (block 3), whereas Zn retention was poor with 26% (block 1) and -26% (block 3). Negative values refer to a higher concentration of Zn in the treated than in the untreated soil. These may be due to a lower pH in block 3 (see Fig. 4.2-1). Explanations for the differences between Cu, Zn and Pb retention may be the stronger affinity of Pb to exchange sites. In addition, CFH-12 and zerovalent Fe contained elevated concentrations of Zn and Cu.

Top application of sorbents was less effective with substantial variation among the elements (Fig. 5.2-1). While 37% of Pb was sorbed with the addition of zerovalent Fe, Sb concentrations barely changed. This is different with CFH-12&limestone. Here, Sb concentrations in porewater decreased (39% retention). The observed sorption deficits of top application were probably due to the absence of downward movement of the Fe-based amendments. The addition of limestone did not have the same effect on pH as it had when mixed in. In block 2, section B, where CFH-12&limestone was added as top application, pH values did not change as they did in B sections of the other three blocks (Fig. 4.4-8). The limestone did therefore not have an effect on pH, showing that downward movement from the top layer was ineffective. Porewater concentrations for Pb, Cu and Zn even showed negative effects of CFH-12&limestone as top application. Two explanations were found for this increase in element concentrations, the first being amendment composition. CFH-12 contains small amounts of Pb, Cu and Zn (Table 3.1-1) which may leach from the top layer of application into the soil below where no sorbent is present. The same probably applies to zerovalent Fe which contains 19µg Sb/kg leading to a small increase of Sb in the porewater. However, the amounts of Cu (6 mg/kg) and Pb (<10 g/kg) contained in CFH-12 are not very

large. Another explanation for substantial Cu, Pb and Zn increase in porewater from amended soil is ion exchange. Competition for sorption sites came primarily from Ca (calcium) ions which, as opposed to the sorbents, leached from the top layer into the soil. Figure 5.2-2 shows that the porewater concentration of Ca increased in all CFH-12&limestone treated sections, not only in the mixed in application. With sorbents missing in the soil below the top layer, no pH increase and similar Ca concentrations as in blocks 1, 3 and 4, the addition of CFH-12&limestone in block 2 was counterproductive. This was slightly different in zerovalent Fe treated soil (block 2), where Cu and Pb retention was low, but not negative. This was probably due to the lack of limestone.

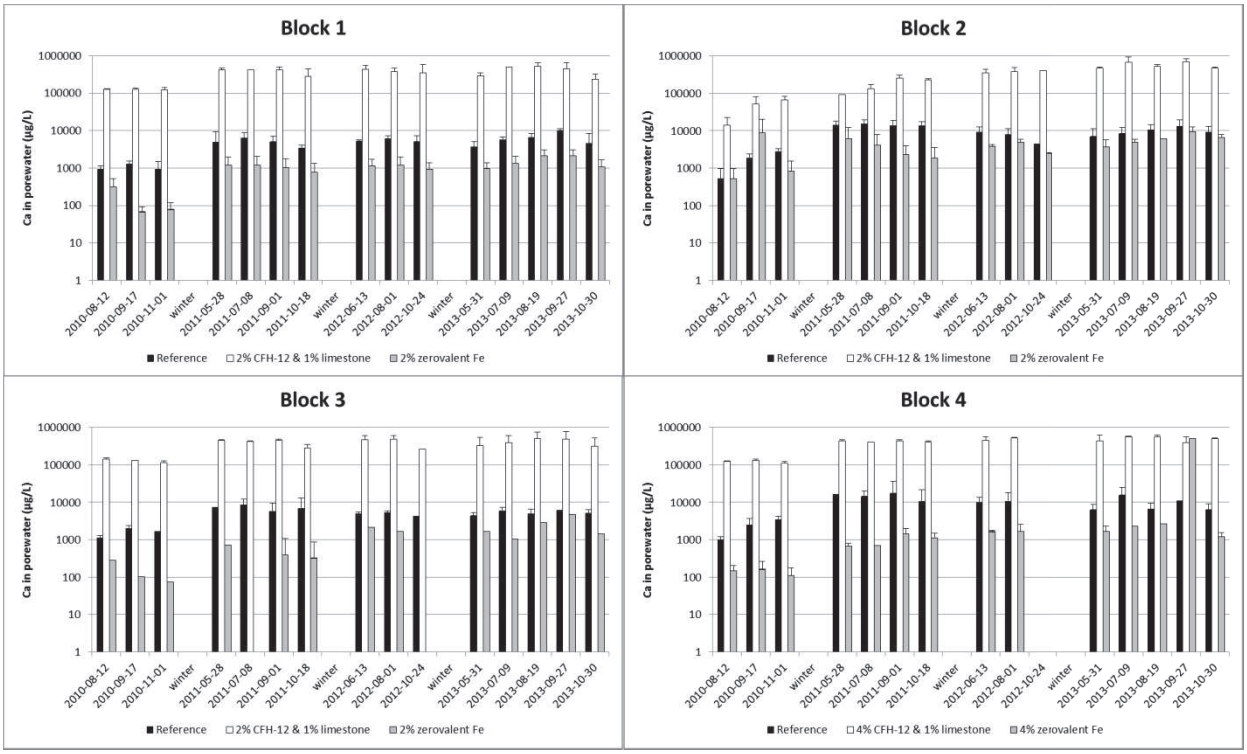

Figure 5.2-2: Average porewater calcium concentrations (2010-2013).

The electric conductivity was measured and confirmed that cation concentrations were similar in both application types (mixed in and top application; Fig. 5.2-3). Electric conductivity increased in all sections with the addition of CFH-12&limestone. Figure 5.2-3 shows a comparison of CFH-12&limestone mixed in (block 1) and CFH-12&limestone as top application (block 2). Electric conductivity started with lower values (~440-2500 µS/cm) in block 2 and higher values (~2900-3600 µS/cm) in block 1 in the beginning of the experiment in 2010. As the values for block 2 increased and for block 1 decreased, they met at approximately the same (~1500-2500 µS/cm) in 2011. All of these values were higher than in soils without CFH-12&limestone (Table B.3-1).

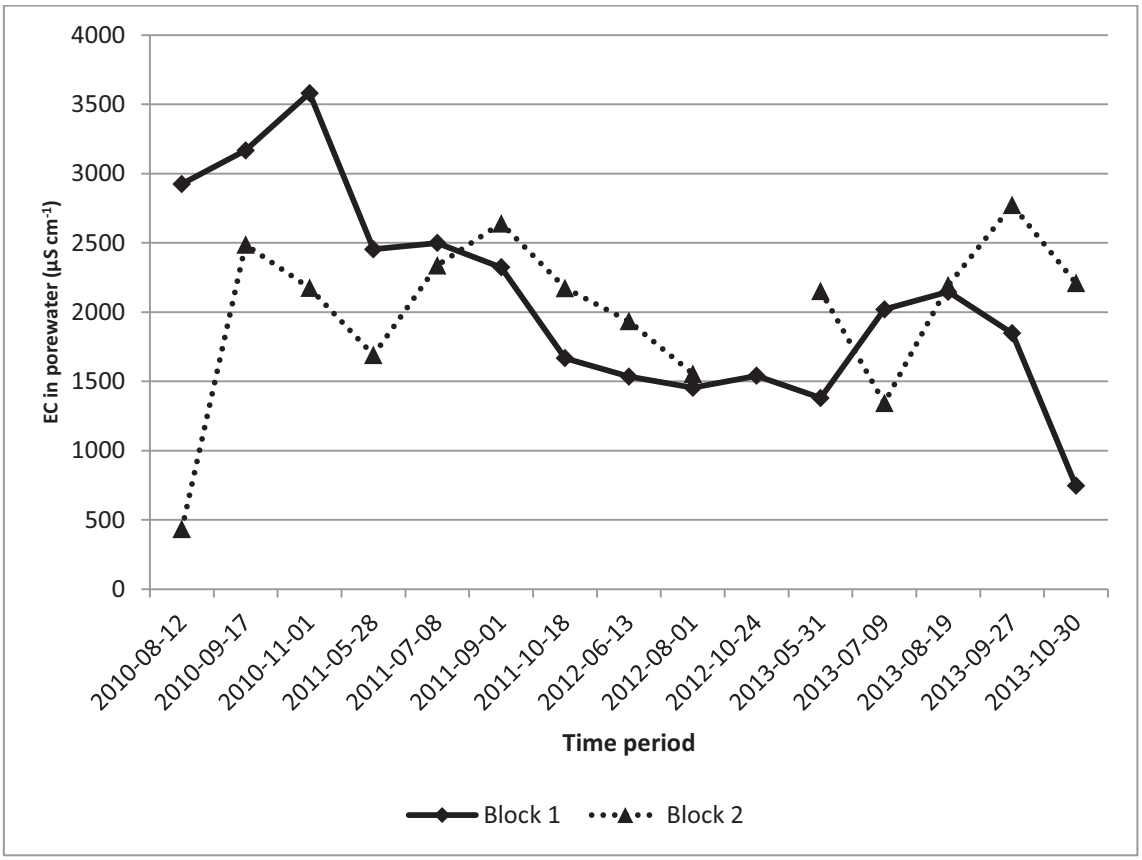

Figure 5.2-3: Average electric conductivity (EC) (µS/cm) in porewater of the CFH-12&limestone treated soil in block 1 (mixed in) and 2 (top application) from 2010-2013.

Element distribution in the soil

The concentration differences in the B sections (Fig. A.1-2) occured in a relatively narrow pH range of 7 – 8, indicating that pH was not responsible for these variations. Not enough data was collected for assessing the role of the DOC content or weathering rates. A possible explanation could be the total heavy metal concentrations in the porewater of the B sections. At pH levels this high, these were generally very low, due to more efficient sorption. For example the Cu concentration ranged from ~1.2 to ~11.3 µg/L. Even lower values of <1 - ~6µg/L were found for Pb. Therefore, the differences were actually not very large, at least where Cu and Pb are concerned. The highest concentrations were found for Sb and Zn, ranging from 3 - 124µg/L and ~7 - ~180µg/L, respectively. Other factors, such as amendment composition and smaller local variations may be responsible for these differences.

Saturation and element speciation

Element retention may occur by sorption or by precipitation of secondary minerals such as Cu carbonates ($CuCO_3$, azurite and malachite (hydrated Cu carbonates), smithsonite $ZnCO_3$, cerussite $PbCO_3$), oxides (tenorite CuO, $Zn(OH)_2$, massicote PbO, $Pb_2O(OH)_2$, SbO_2) and

iron minerals. Like the XRD analysis, geochemical modeling indicated no formation of the expected minerals. The saturation indices calculated by Visual MINTEQ usually had values below zero, hence they were undersaturated. This means that the retention effect in treated soil waters was due to sorption, not precipitation of minerals. The saturation indices can be seen in Table B.2-1 in the appendix. Saturation indices modeled for other samples are not shown, because they are not significantly different.

Lead and copper were to ~100% bound to DOC in the treated soils of block 1, sections B (CFH-12&limestone) and C (zerovalent Fe) (Fig. 5.3-1 and 4.5-2). The pH increase in section B facilitated the complexation with DOC, but it was not the only factor. The sorption of the elements by the amendments decreased their concentration in the porewater, leaving a much higher DOC to element ratio in the solution. The relatively small Pb and Cu content then had a large amount of DOC for ligands. In the reference soil, Cu was mainly bound to FA1 (fulvic acids with carboxylate groups), but in CFH-12&limestone FA2 (fulvic acids with phenolate groups) was dominating (>90%). This may be caused by the higher pH.

In contrast to Pb and Cu complexation, Zn occurred primarily as Zn^{2+} in CFH-12&limestone treated soil water, as seen in Figure 5.3-1, although Zn is expected to primarily form complexes with DOC above pH 6.5 (chapter 2.1 Element properties). The cause for this could be competition from Cu and Pb for fulvic acids, because Pb and Cu may have a higher affinity to DOC than Zn.

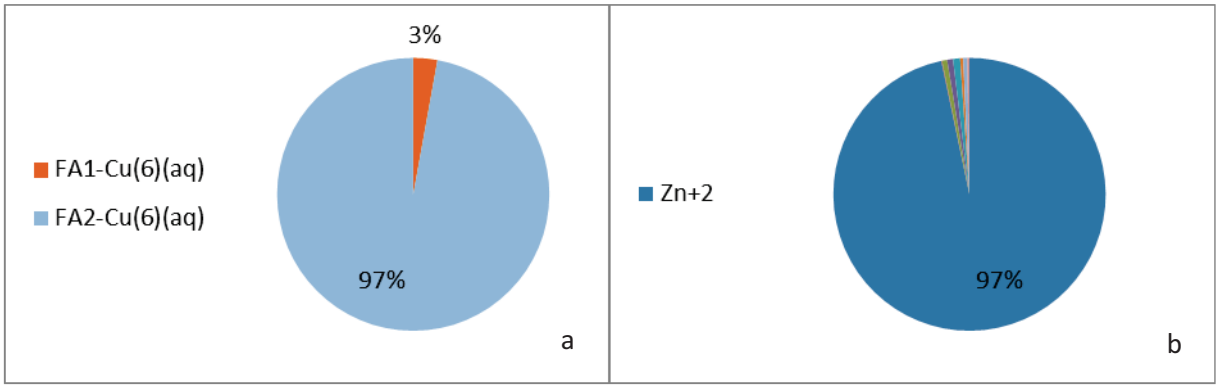

Figure 5.3-1: Cu and Zn speciation in block 1, section B (CFH-12&limestone), pH = 7.51. a: Cu speciation, b: Zn speciation. Other species were calculated, but their percentages were very low (< 1%). They are not shown in these charts. FA1 = fulvic acid containing carboxylate; FA2 = fulvic acid containing phenolate anions. Sampling day: 9/27/2013.

6. Conclusions

Very high concentrations of Cu, Zn, Pb and Sb are present in Steinsjøen shooting range soil caused by the weathering of spent bullets. The concentrations in the soil porewater did not change from 2010-2013 indicating constantly high weathering rates. Element concentrations in untreated soil were higher than normal background values and EU drinking water limits. Concentrations in surface waters were also substantial, though not quite as high as in the porewater of the stop butt soil. According to Norwegian EQS values, Pb and Cu concentrations in downstream creek water could be classified as "strongly contaminated" (condition IV of V).

Speciation of Pb and Cu showed a dependence on pH and DOC content. In porewater with high pH and a high DOC concentration, the two metals were primarily bound to fulvic acids. Lead preferred complexation with fulvic acids containing phenolate anions, Cu with fulvic acids containing carboxylate anions. Zinc occurred primarily as Zn^{2+}, Sb as antimonate ($Sb(OH)_6^-$).

Seasonal variations could be found monitoring the porewater of stop butt soil, where element concentrations were generally higher in the month July and August than in May, June, September and October. Possible reasons are dilution caused by larger amounts of added water due to the snow melt in spring and heavy rains in autumn, an increased weathering rate due to higher temperatures and pH changes. A correlation between pH and element concentrations was difficult to confirm, but the general trend could be seen in parts of the data.

Porewater from soil mixed with 2% CFH-12&limestone showed increased pH due to the limestone, and a very good retention for Pb (>94%) and a moderate retention for Sb (59-74%), Cu (64-70%) and Zn (60-73%). In soil mixed with 4% CFH-12&limestone, Sb retention was higher (>85%) despite higher pH. Lead (>94%), zinc (>70%) and copper (>74%) retention was in the same range as for 2% amendment.

Porewater concentrations in soil mixed with 2% zerovalent Fe also showed similarly good retention for Pb (>94%), Cu (> 46%) and Sb (~73%). However, Zn retention was very low (26%) and negative (-26%). Copper concentrations in soil mixed with 4% zerovalent Fe increased drastically, probably due to ion exchange reactions with Ca and the addition of Cu contained in the amendment.

The results show that mixing the amendments into the soil is preferable compared to top application which had lower stabilization efficiency for Sb (~40%) and a negative effect on Pb, Cu and Zn. While pH values have not changed with the top application of CFH-12&limestone, Ca concentrations increased strongly resulting in ion exchange reactions and the mobilization of Cu, Pb and Zn. CFH-12 itself contains Zn, and probably contributed to higher concentrations in the sections with top application. Top application of zerovalent Fe resulted in very low retention for the metals and a small input of Sb, possibly due to pH changes.

The detection limit for Fe minerals, oxides and carbonates was too high for the XRD analysis to be helpful in determining the presence of secondary minerals. Goethite and birnessite could be identified, but not very clearly. It is therefore advised to use different techniques such as Raman spectroscopy for this purpose.

The Fe-based amendments CFH-12&limestone and zerovalent Fe are both promising stabilization methods for the contaminants Pb, Cu, Zn and Sb in shooting range soils. Since the weathering rate has not been decreasing, retention percentages indicate that the stabilization efficiency of both amendments have not changed substantially from 2010 to 2013.

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Appendix

A Figures

A.1 Concentration vs. pH plots

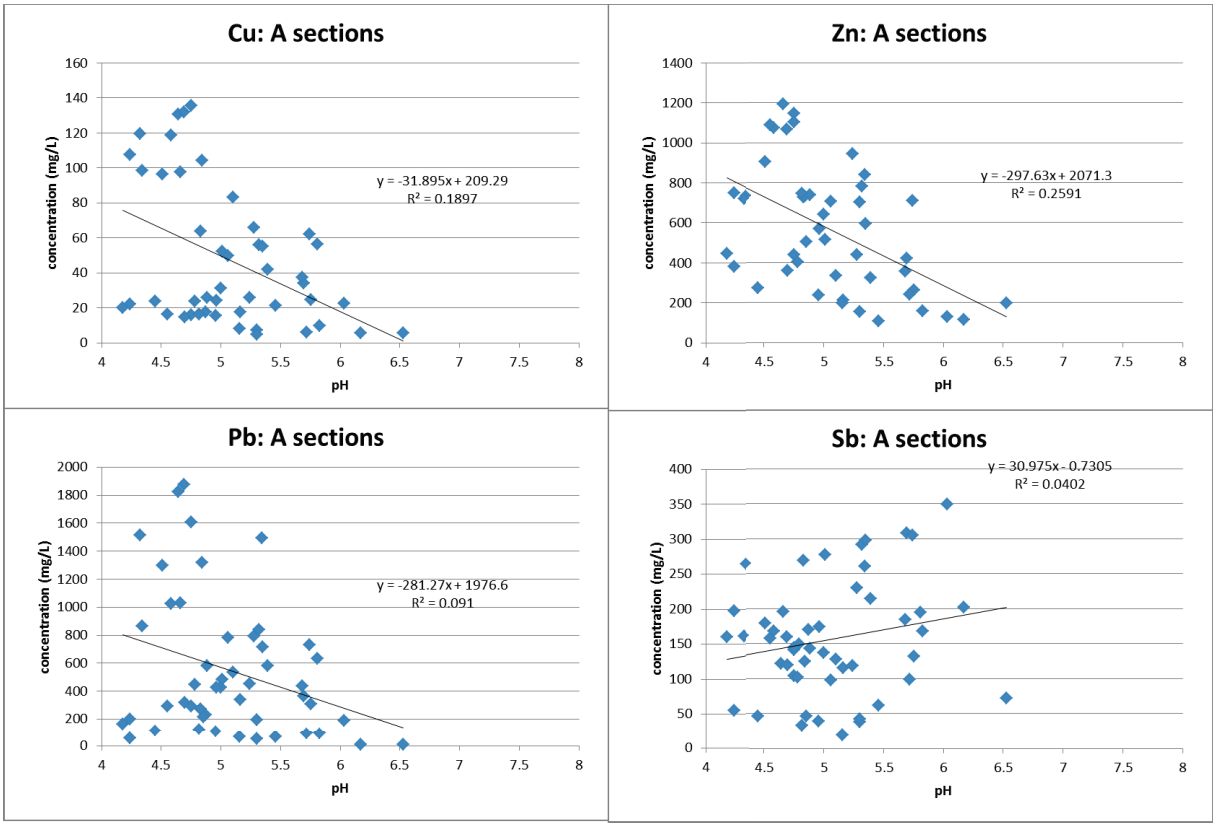

Figure A.1-1: Cu, Zn, Pb and Sb concentrations plotted vs. pH. Sections A from blocks 1, 3 and 4.

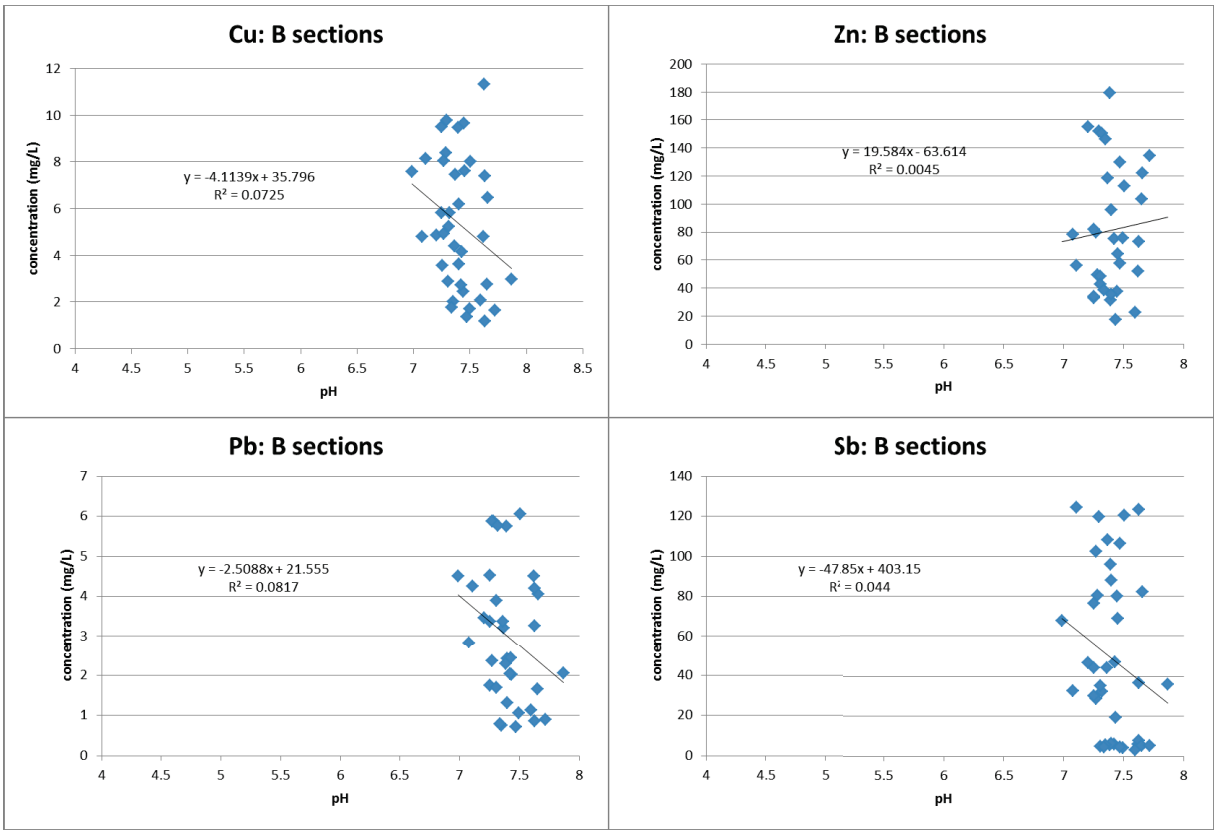

Figure A.1-2: Cu, Zn, Pb and Sb concentrations plotted vs. pH. Sections B from blocks 1, 3 and 4.

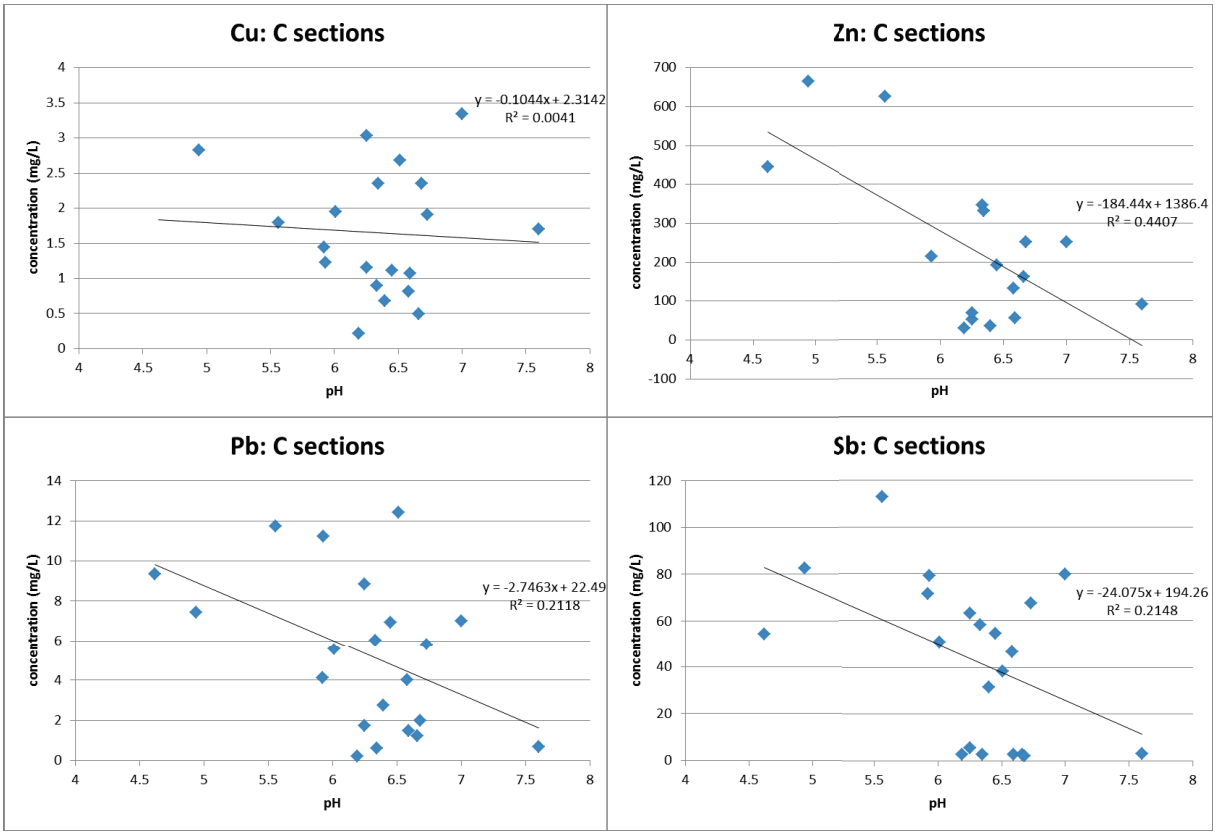

Figure A.1-3: Cu, Zn, Pb and Sb concentrations plotted vs. pH. Sections C from blocks 1, 3 and 4.

A.2 Speciation diagrams

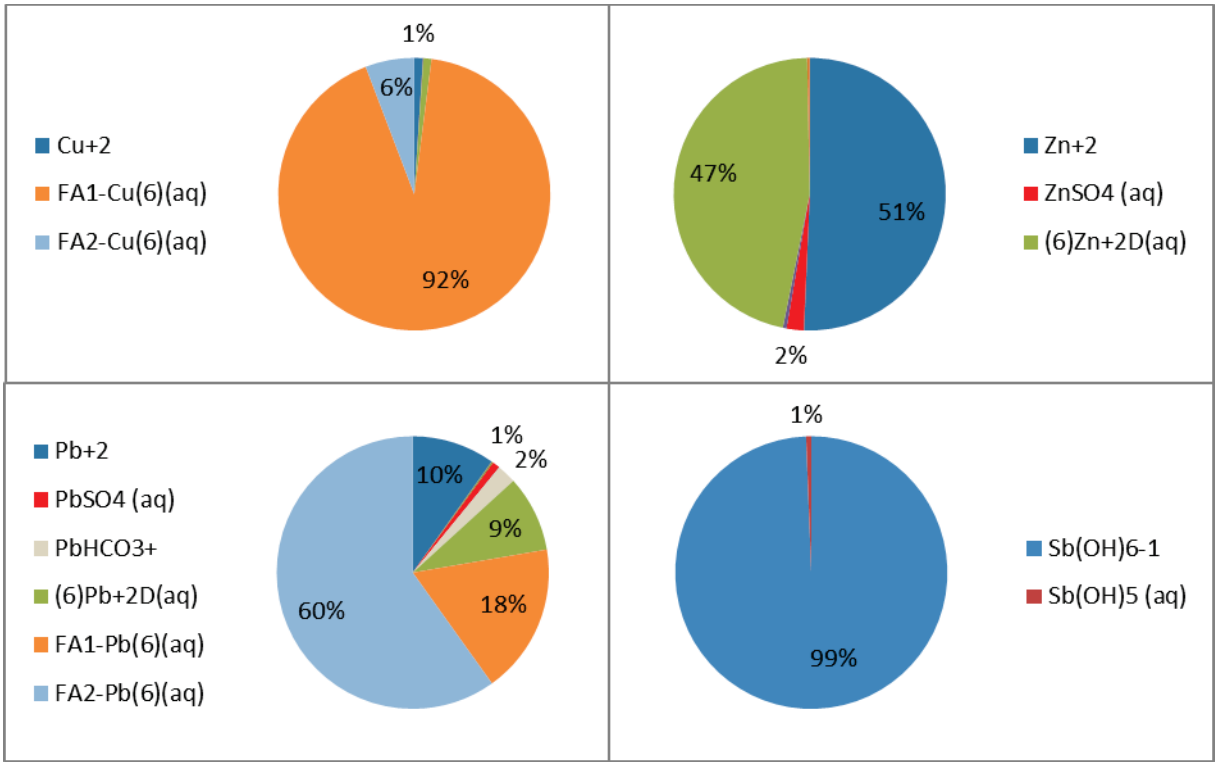

Figure A.2-1: Block 1, section A, pH = 5.0. DOC = 17.2 mg/L. [Cl⁻] = 23.64 mg/L. [SO_4^{2-}] = 7.84 mg/L. Sampling date: 31-5-2013.

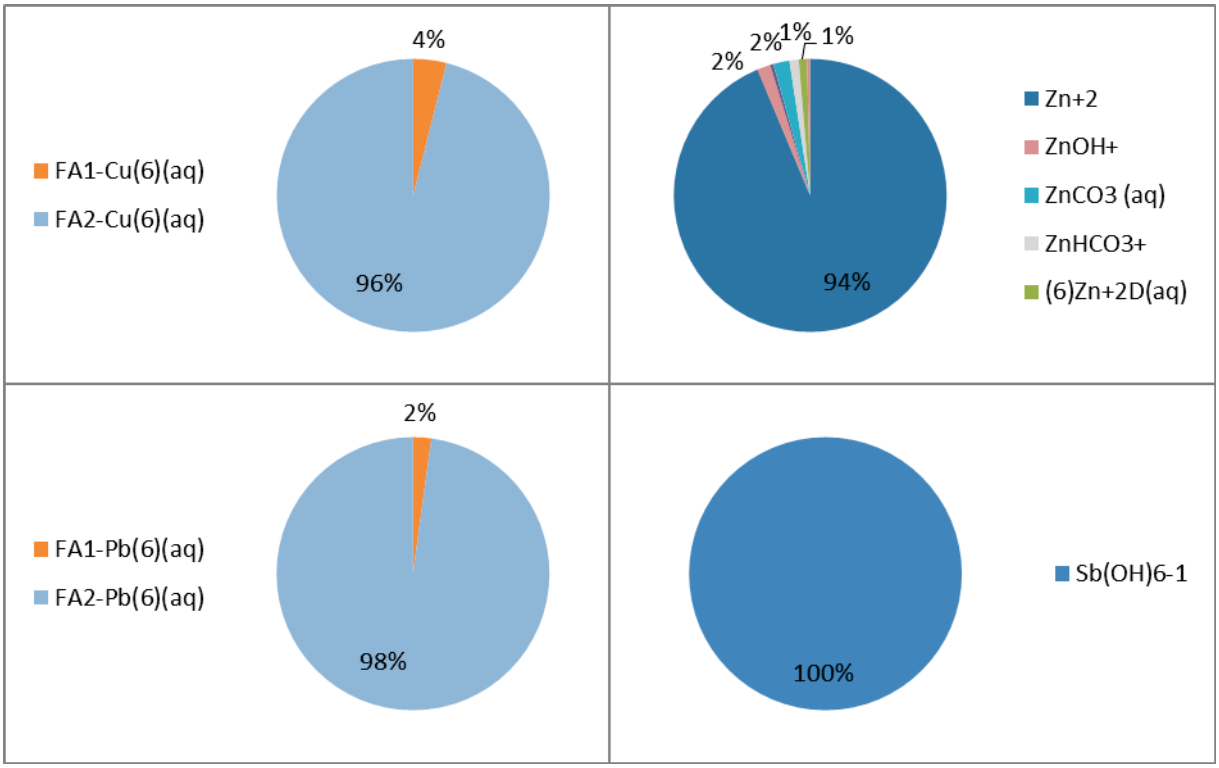

Figure A.2-2: Block 1, section B, pH = 7.37. Sampling date: 31-5-2013.

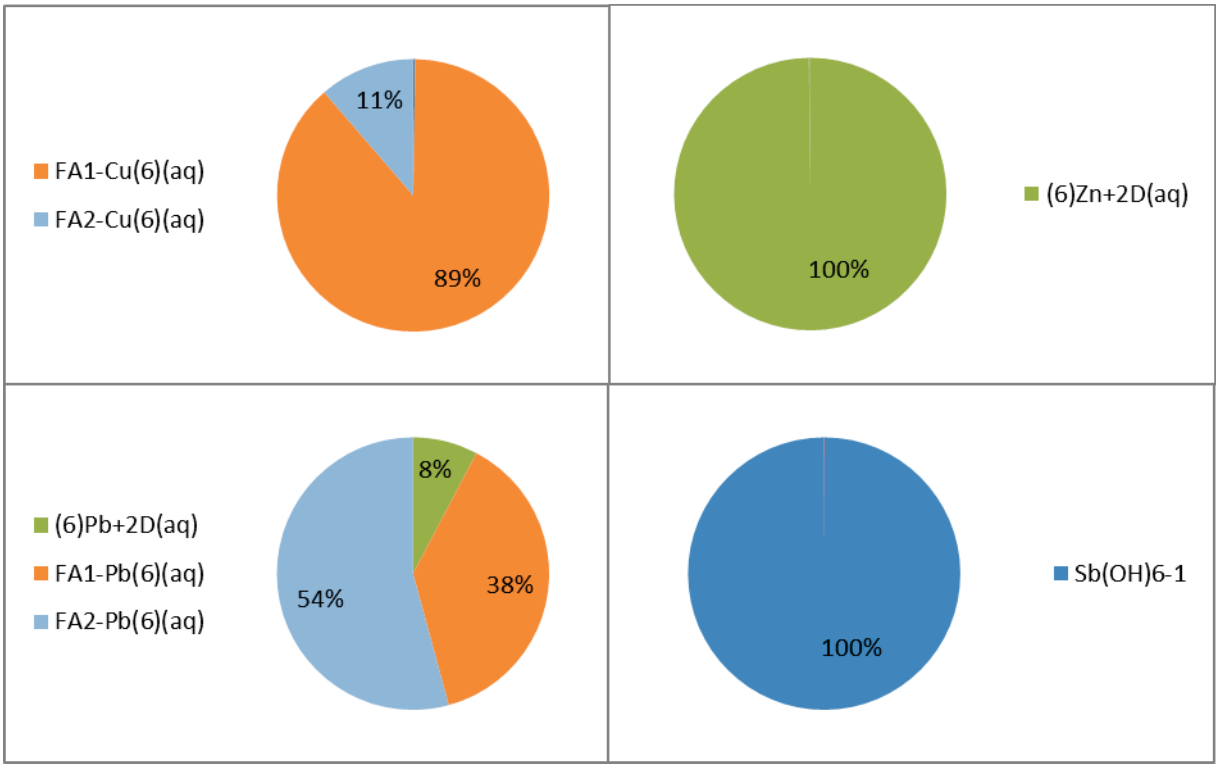

Figure A.2-3: Block 1, section C, pH = 6.01. Sampling date: 31-5-2013.

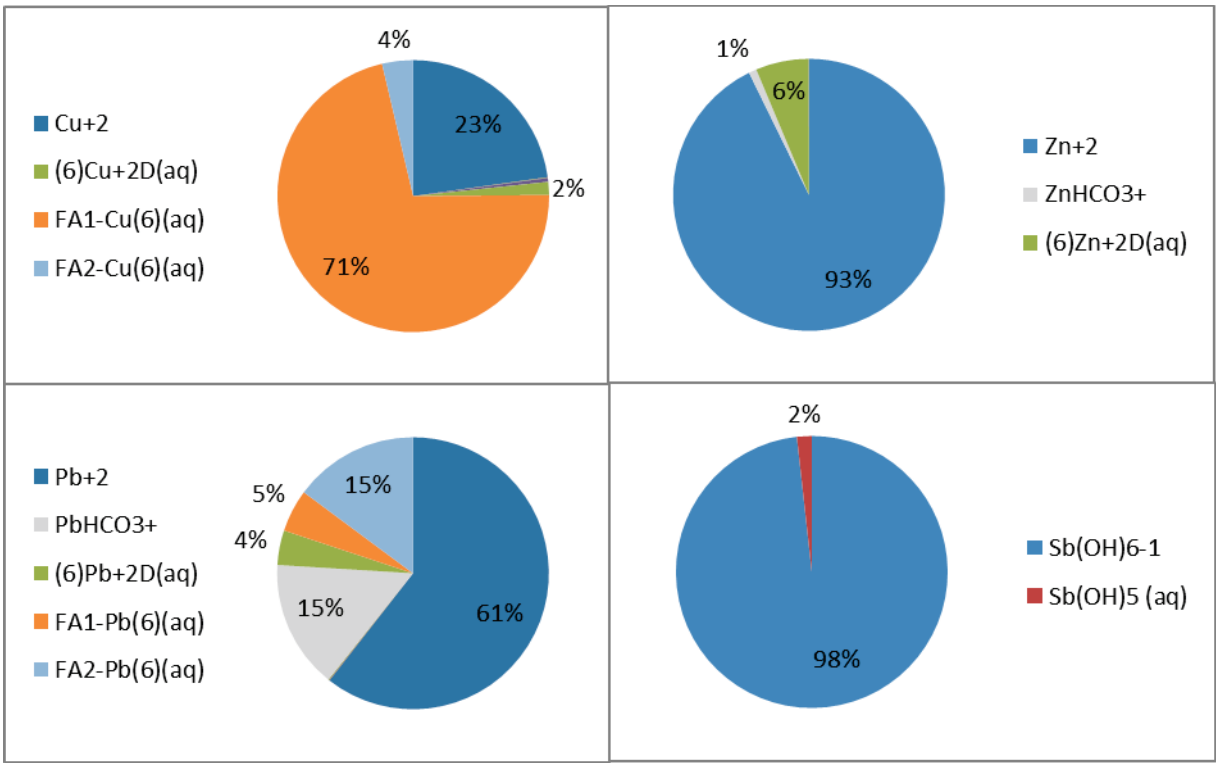

Figure A.2-4: Block 3, section A, pH = 4.6. Sampling date: 31-5-2013.

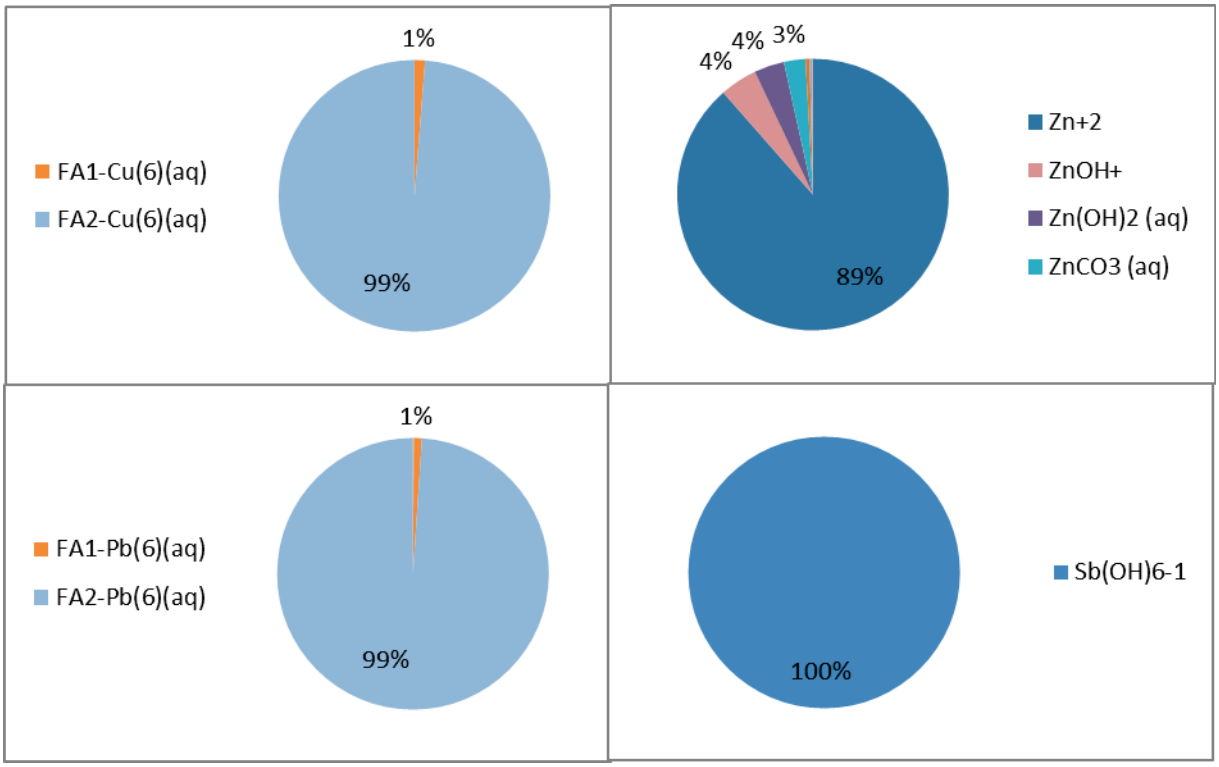

Figure A.2-5: Block 3, section B, pH = 7.87. Sampling date: 31-5-2013.

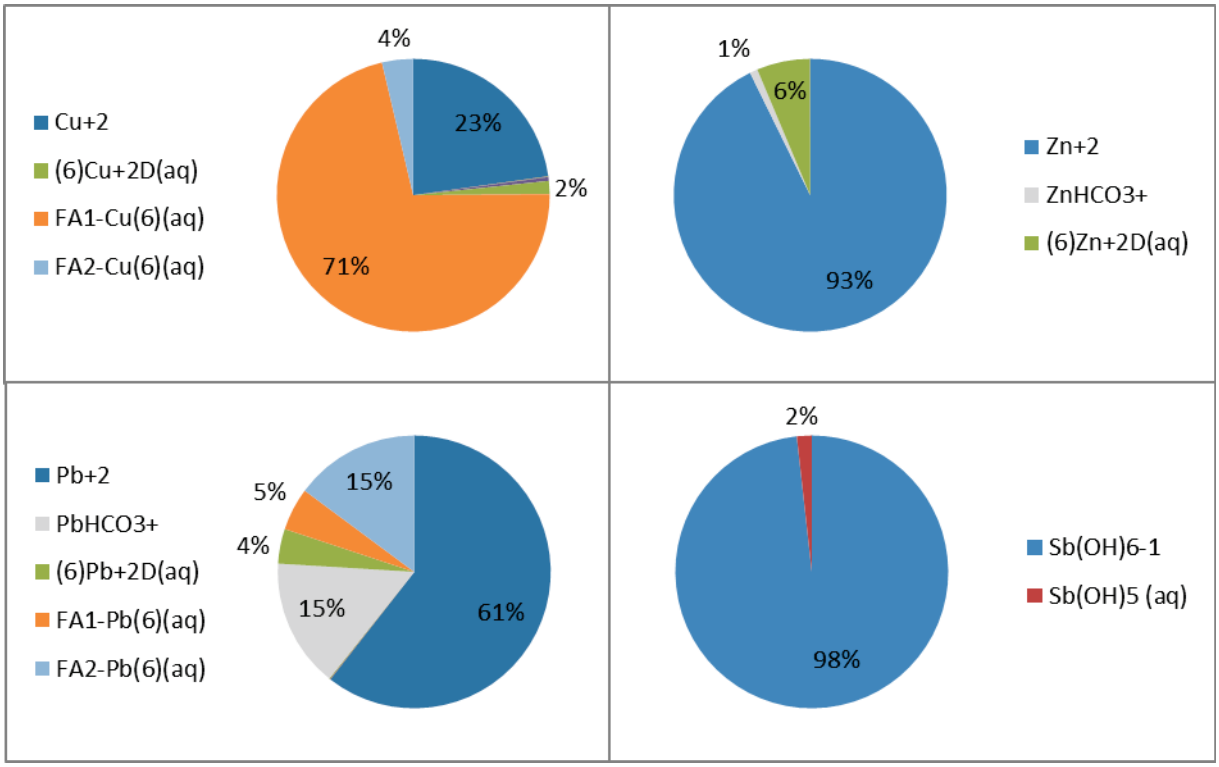

Figure A.2-6: Block 4, section A, pH could not be measured. Sampling date: 31-5-2013.

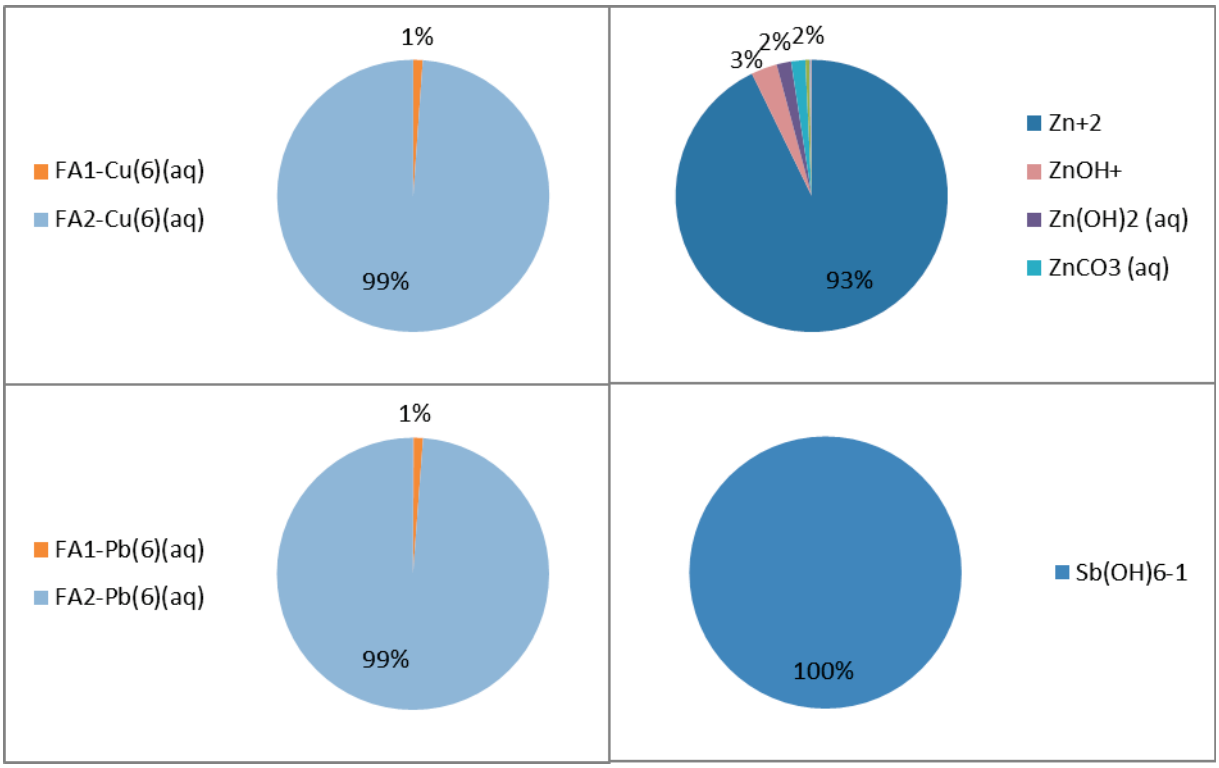

Figure A.2-7: Block 4, section B, pH = 7.72. Sampling date: 31-5-2013.

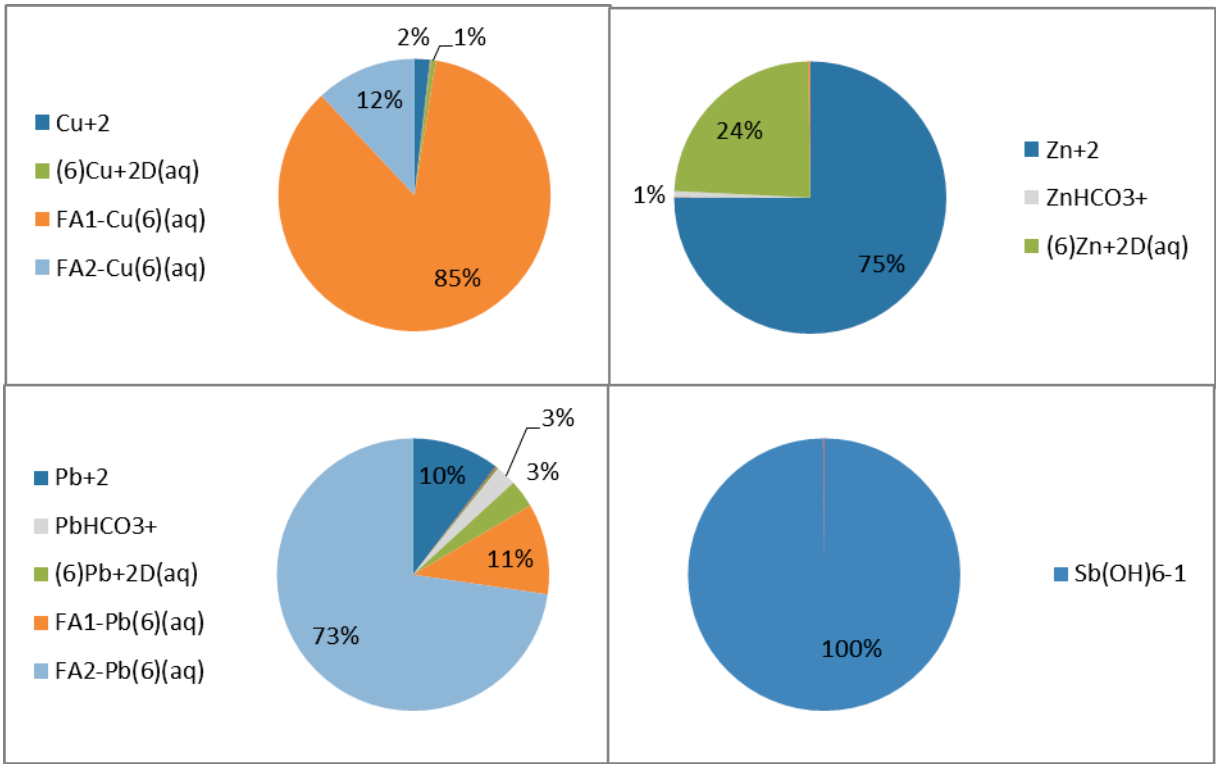

Figure A.2-8: Block 1, section A, pH = 5.74. Sampling date: 9-7-2013.

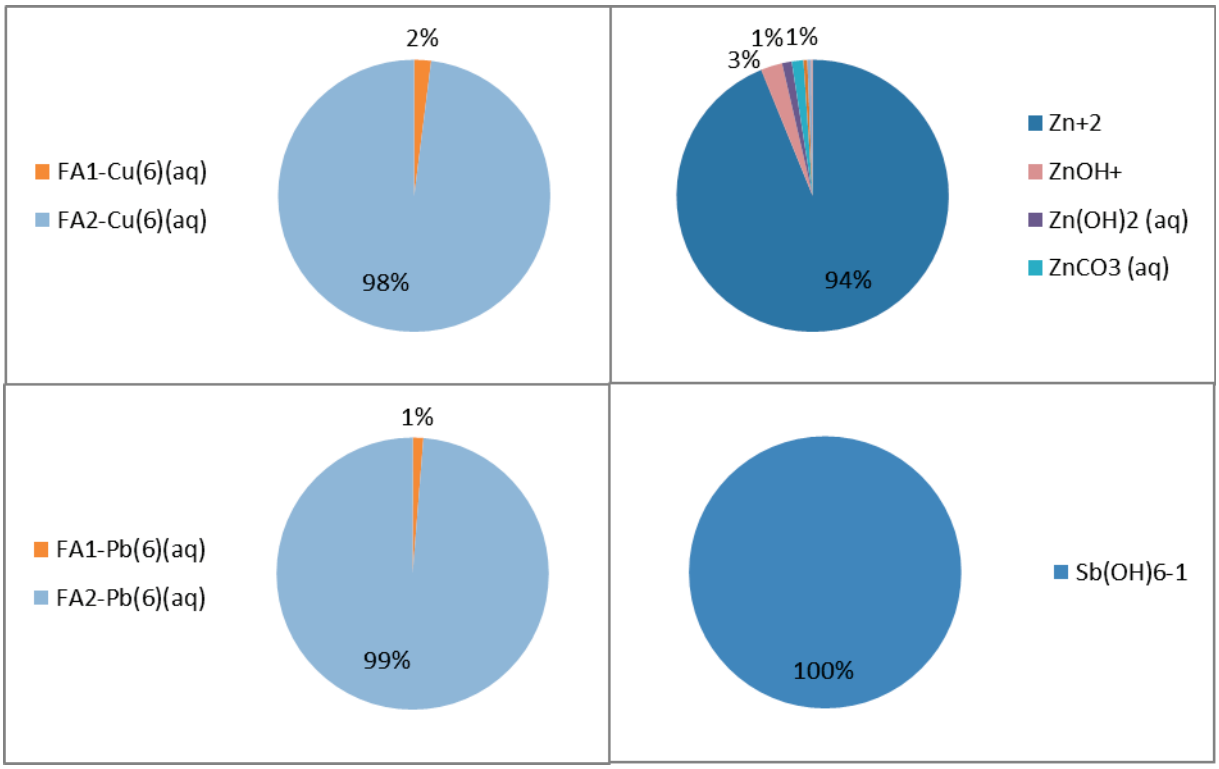

Figure A.2-9: Block 1, section B, pH = 7.63. Sampling date: 9-7-2013.

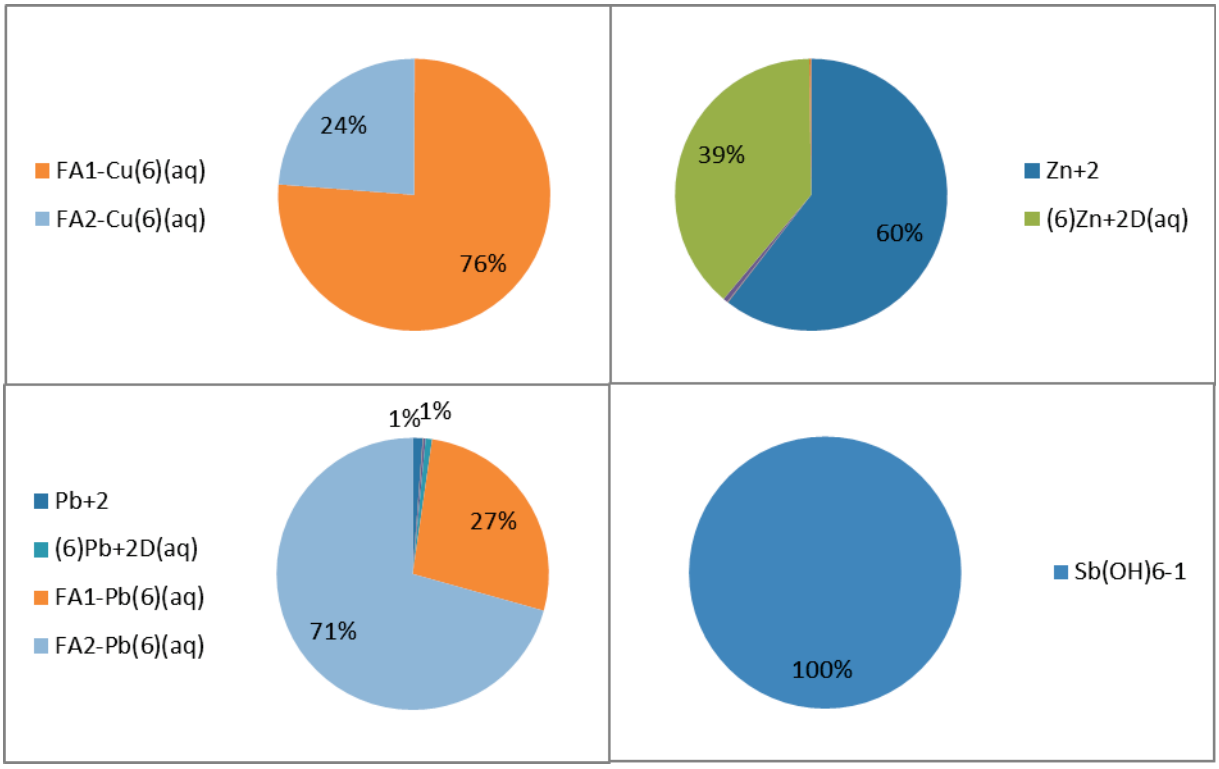

Figure A.2-10: Block 1, section C, pH = 5.92. Sampling date: 9-7-2013.

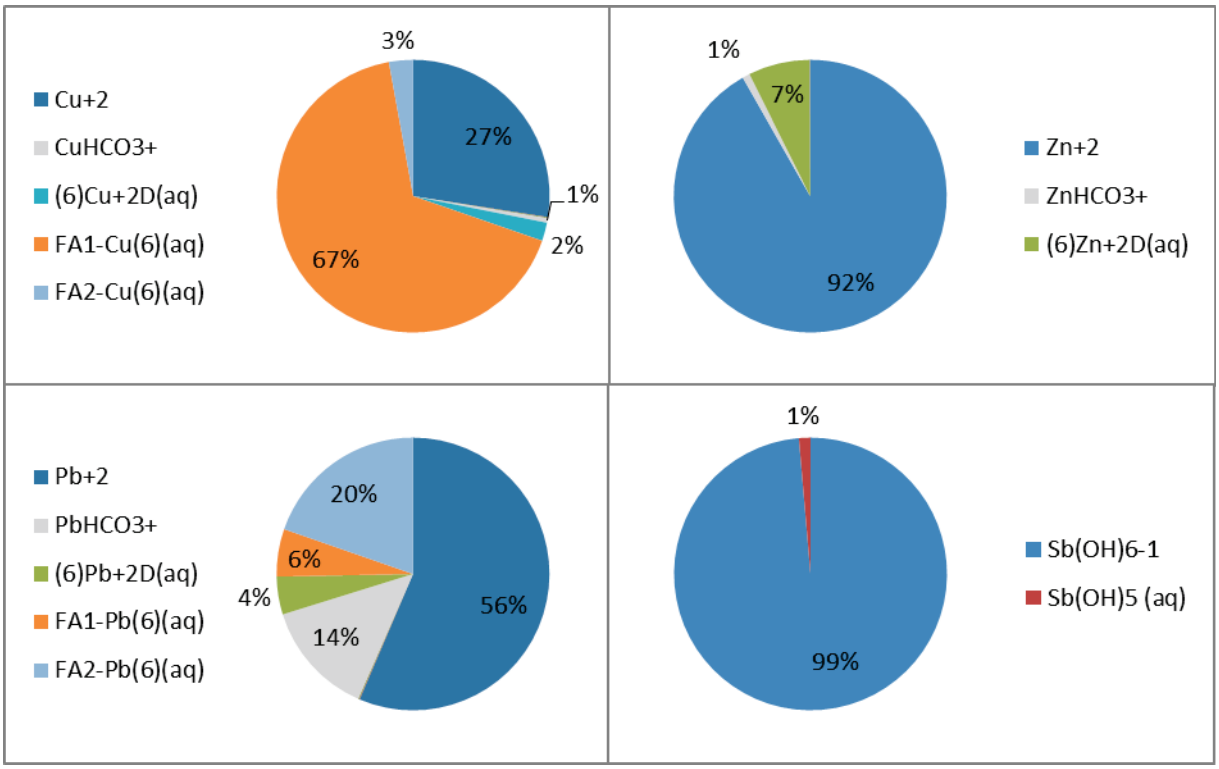

Figure A.2-11: Block 2, section A, pH = 4.66. Sampling date: 9-7-2013.

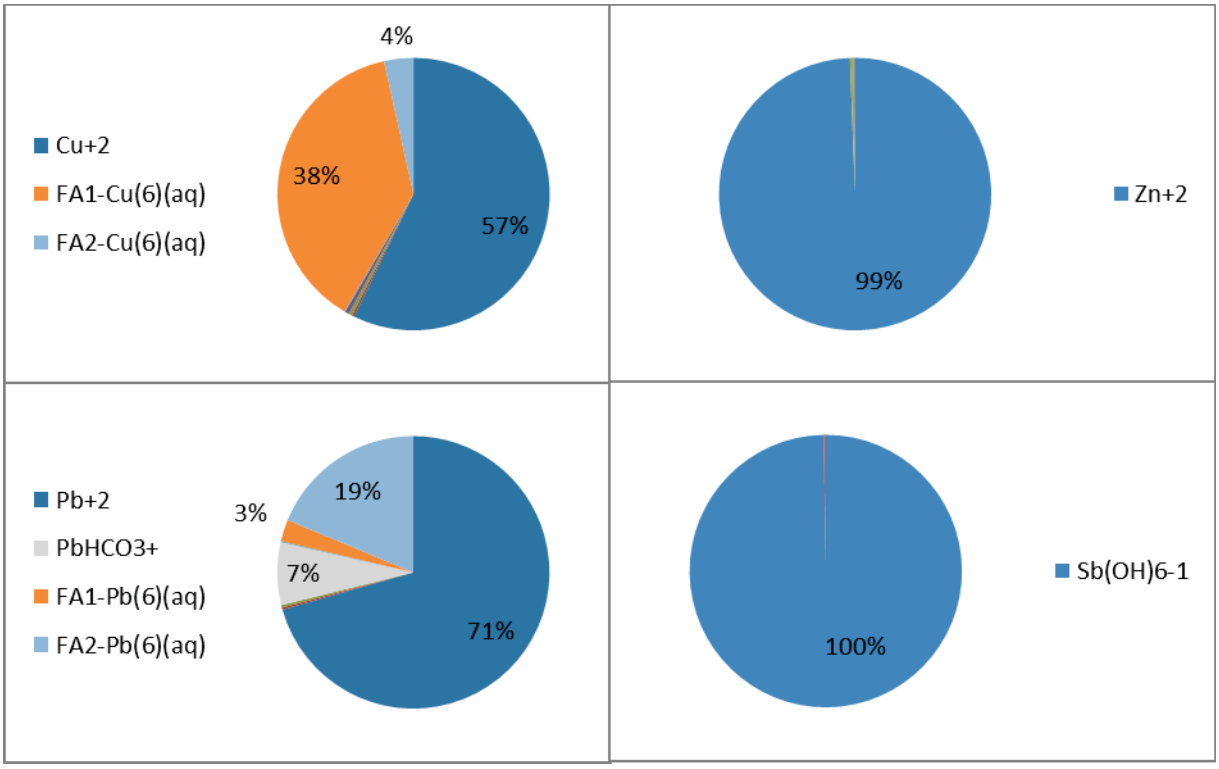

Figure A.2-12: Block 2, section B, pH = 5.38. Sampling date: 9-7-2013.

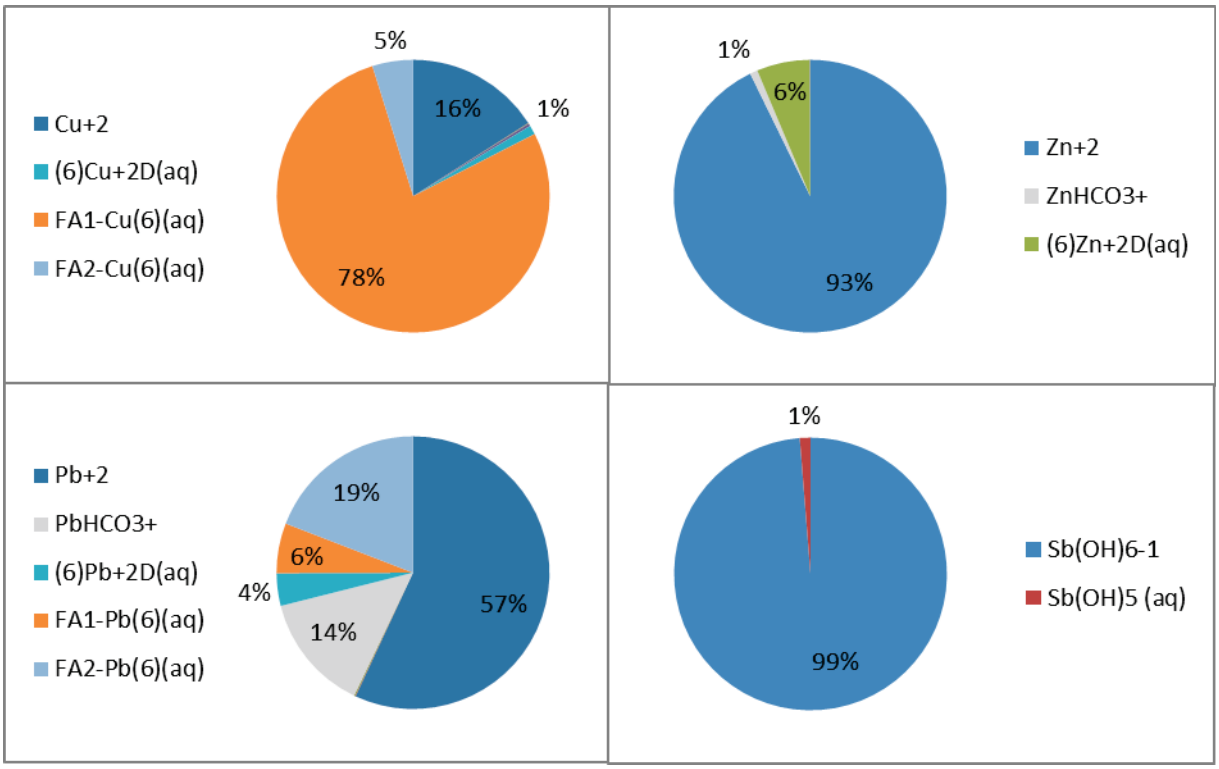

Figure A.2-13: Block 3, section A. Sampling date: 9-7-2013.

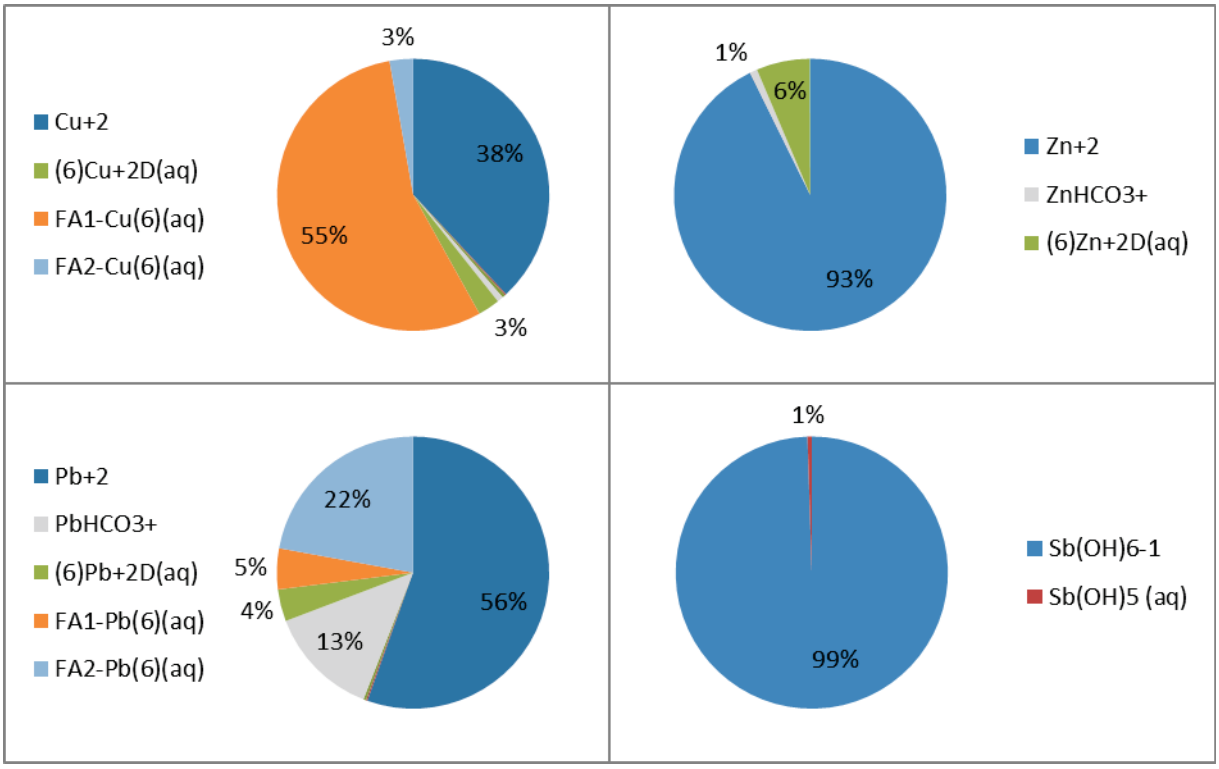

Figure A.2-14: Block 1, section A, pH = 5.1. Sampling date: 30-10-2013.

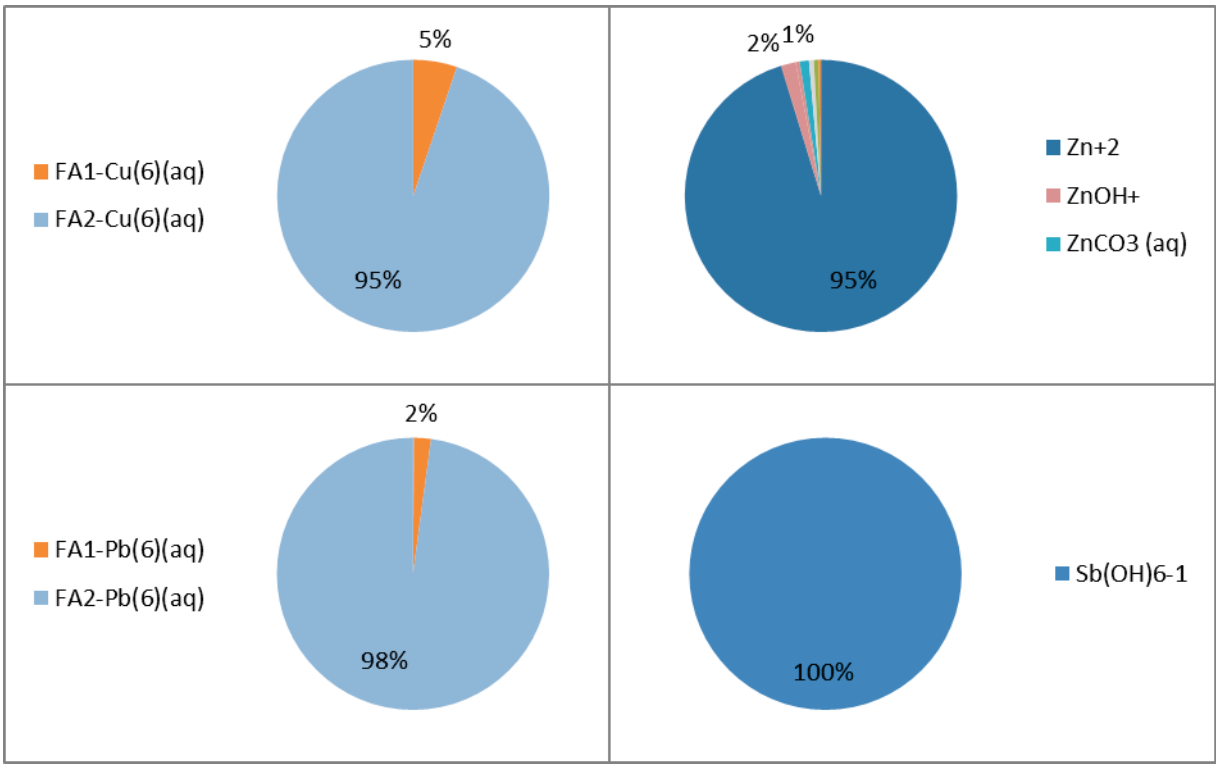

Figure A.2-15: Block 1, section B, pH = 7.4. Sampling date: 30-10-2013.

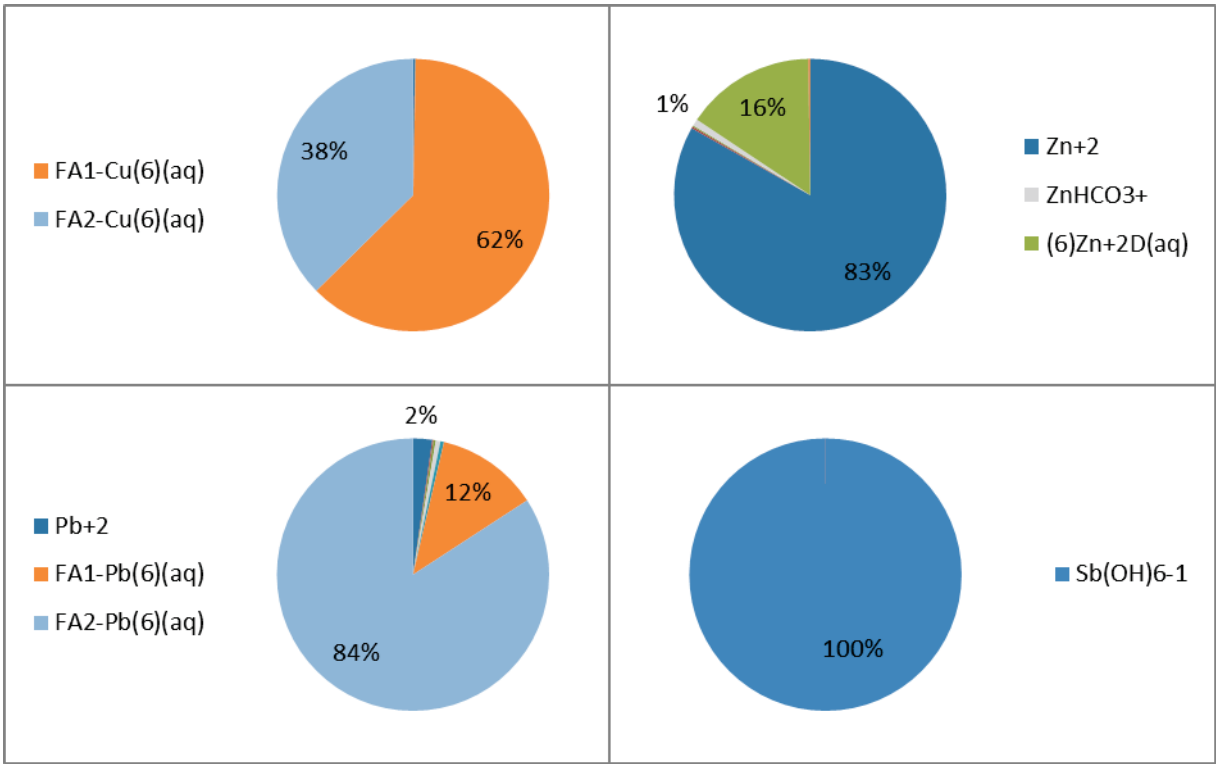

Figure A.2-16: Block 1, section C, pH = 6.4. Sampling date: 30-10-2013.

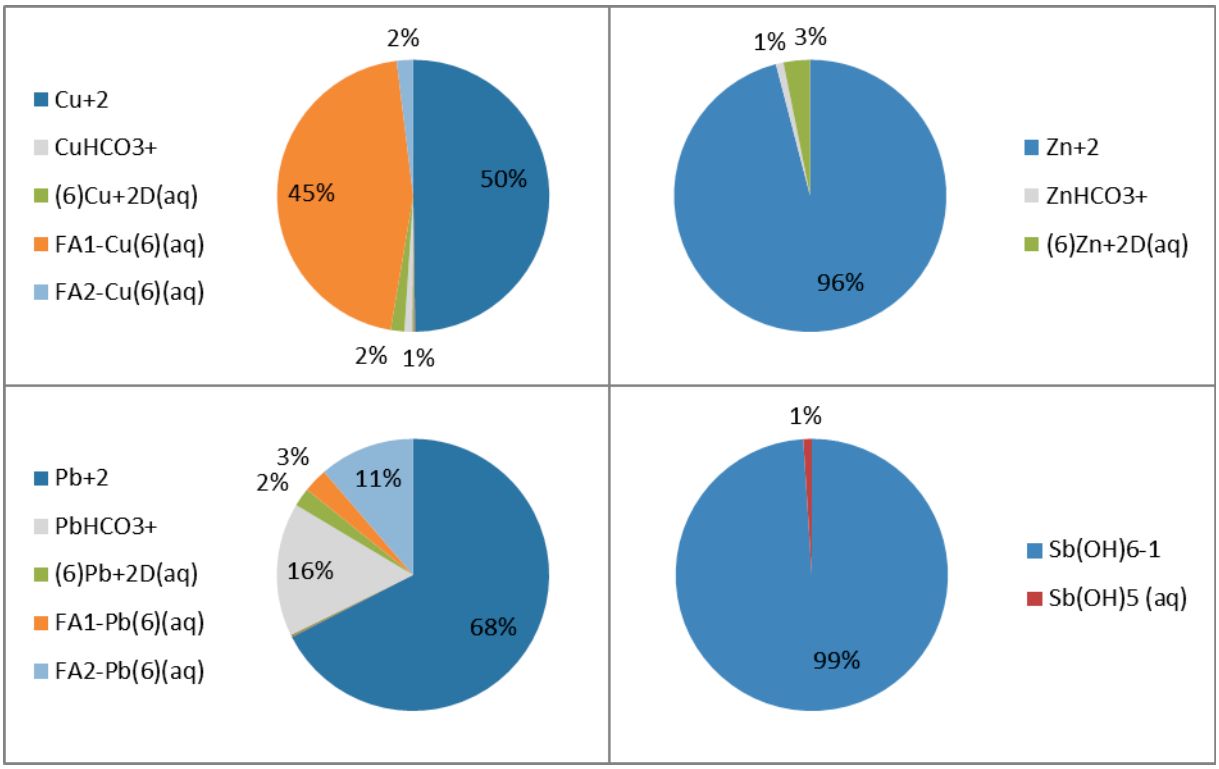

Figure A.2-17: Block 2, section A, pH = 4.8. Sampling date: 30-10-2013.

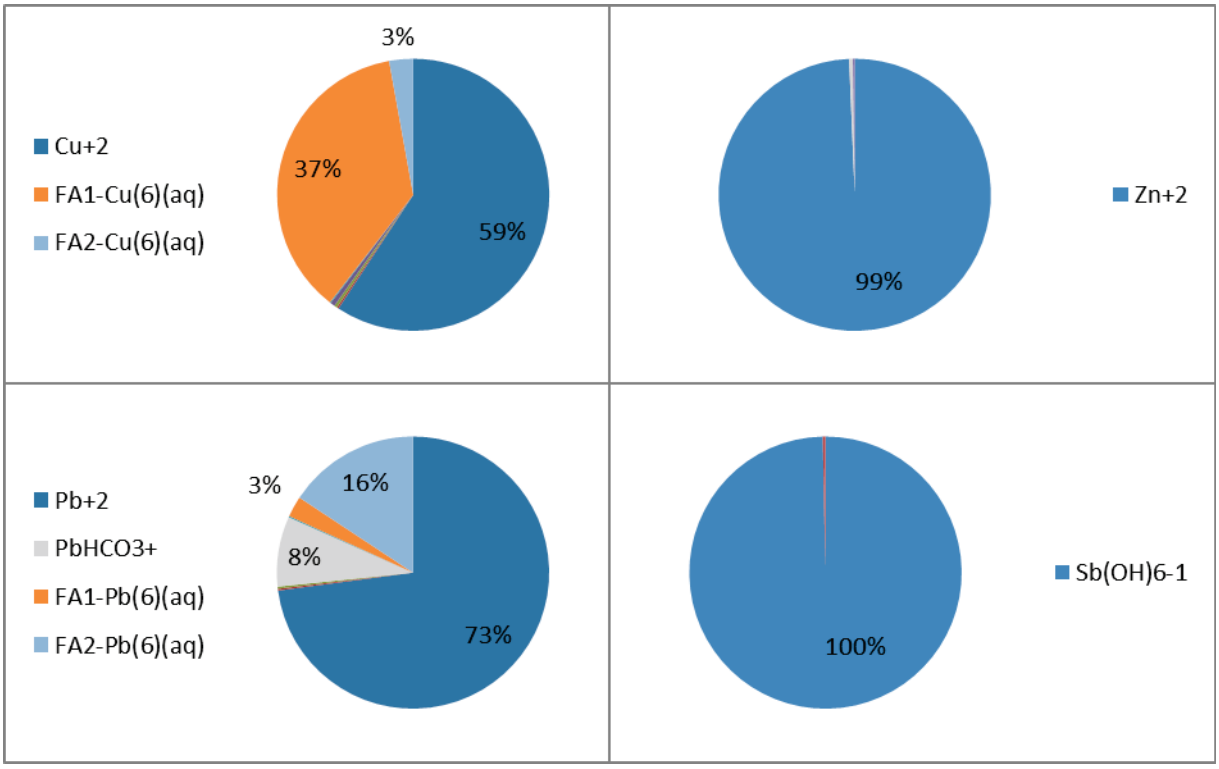

Figure A.2-18: Block 2, section B, pH = 5.25. Sampling date: 30-10-2013.

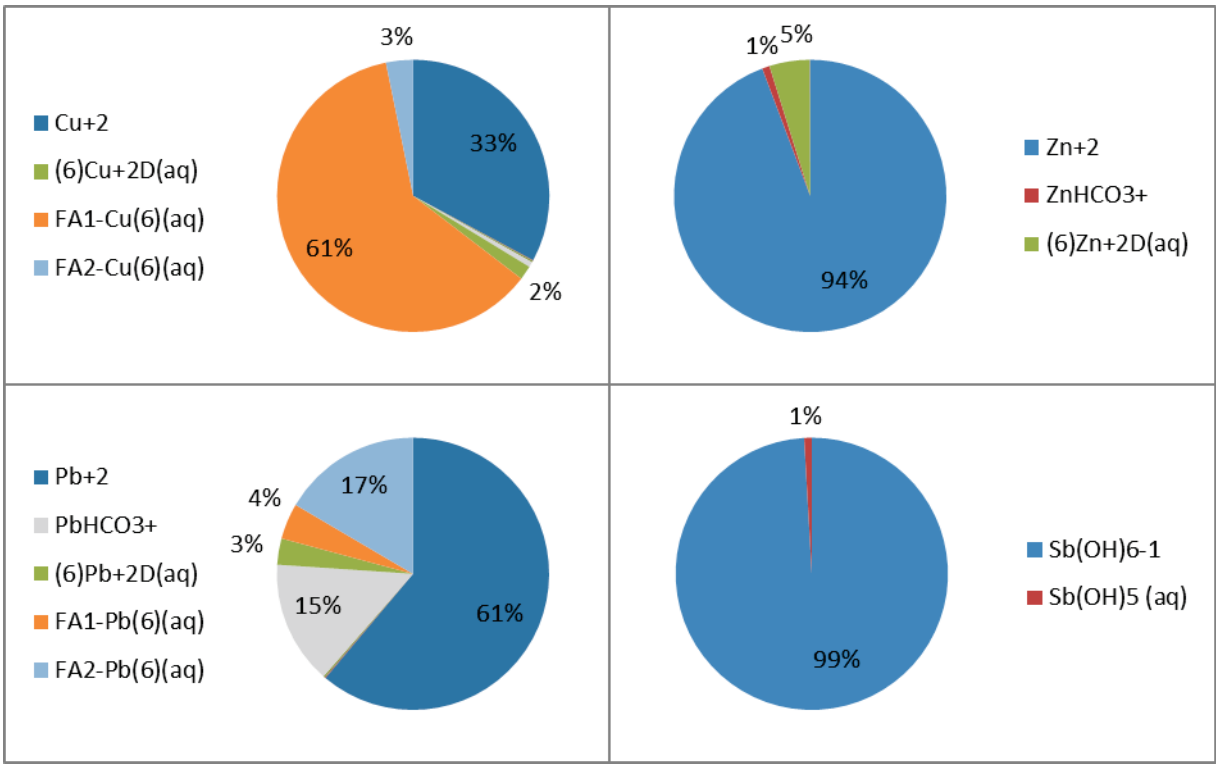

Figure A.2-19: Block 2, section C, pH = 4.85. Sampling date: 30-10-2013.

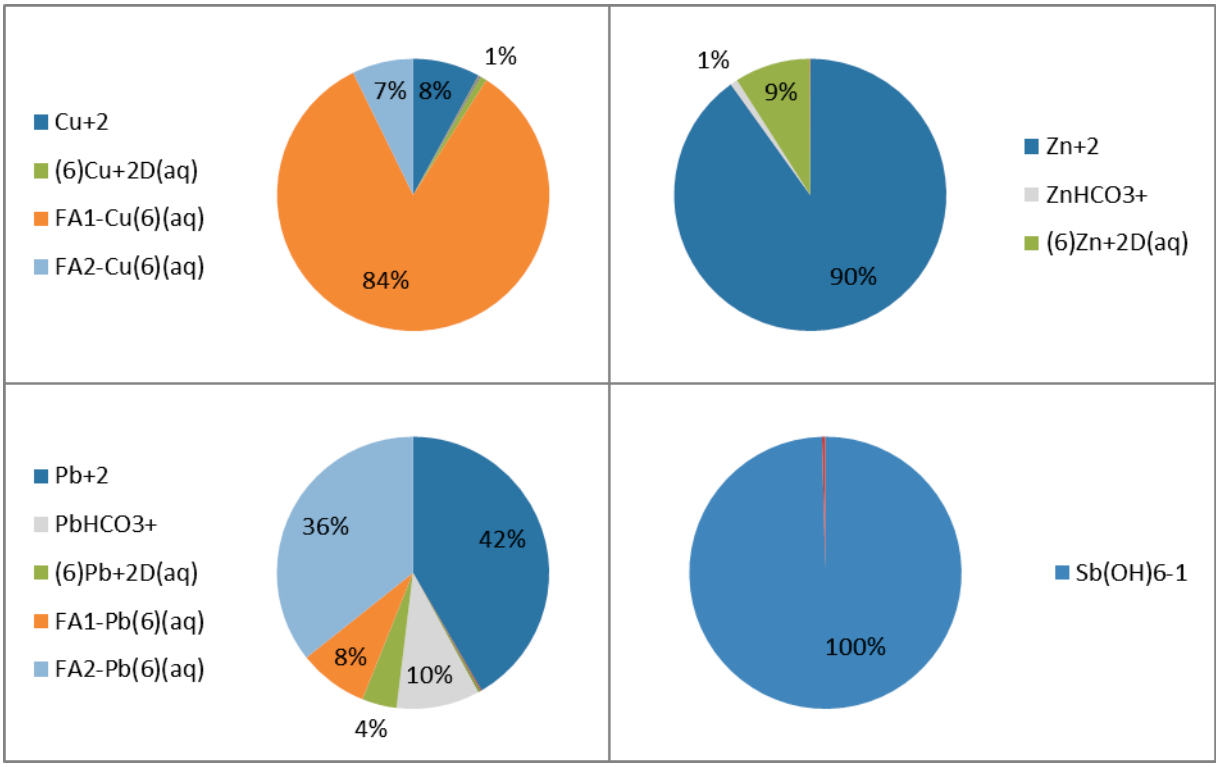

Figure A.2-20: Block 3, section A, pH = 5.2. Sampling date: 30-10-2013.

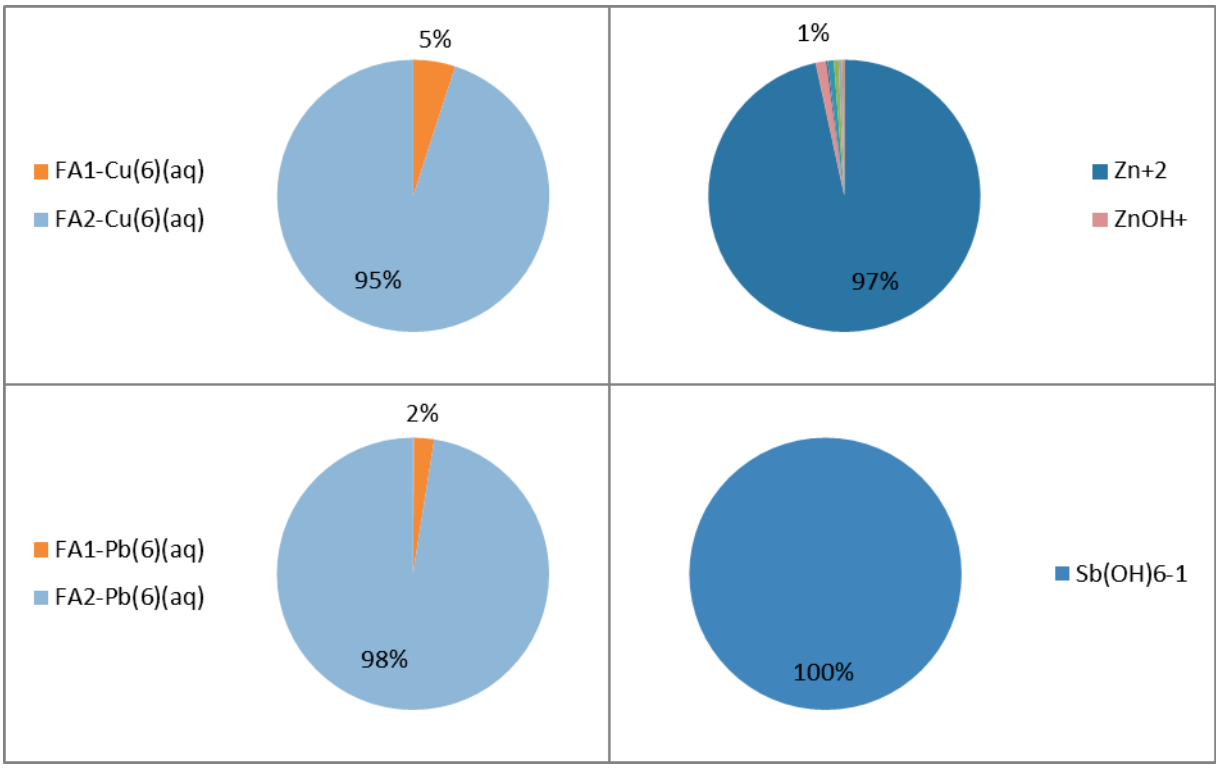

Figure A.2-22: Block 3, section B, pH = 7.25. Sampling date: 30-10-2013.

B Tables

B.1 Water concentrations

Reference

Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	2013-05-31	2013-07-09	2013-08-19	2013-09-27	2013-10-30
Block 1	946	1290	944	5006	6379	5084	3478	5286	6020	5021	3716	5759	6670	10138	4598
Block 2	526	1828	2744	14082	15363	13693	13555	8953	7844	4353	7013	8357	10346	13301	9275
Block 3	1135	1985	1659	7218	8482	5703	6824	4975	5270	4245	4400	5967	4839	6052	5113
Block 4	993	2444	3371	15925	14420	17247	10508	9915	10704		6276	15432	6627	10900	6232

CFH-12&limestone

Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	2013-05-31	2013-07-09	2013-08-19	2013-09-27	2013-10-30
Block 1	128567	126967	123361	428667	422833	428100	288200	437067	384933	353683	289333	497350	530200	456533	239358
Block 2	14192	51297	66857	92275	134050	255000	227467	345967	381950	414400	468733	669867	517067	693467	474205
Block 3	140212	130321	115600	448850	421800	454133	282033	466800	486633	261900	332567	390567	512433	492133	315109
Block 4	121667	134967	112100	436300	410300	429967	408867	447433	521533		429833	563200	568033	396133	502506

Zerovalent Fe

Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	2013-05-31	2013-07-09	2013-08-19	2013-09-27	2013-10-30
Block 1	320	68	79	1185	1197	1046	766	1145	1211	932	969	1337	2131	2170	1078
Block 2	519	8709	826	6166	4172	2288	1874	3788	4915	2522	3695	4861	6206	9425	6608
Block 3	279	102	75	715	0	398	321	2116	1637		1675	1029	2843	4791	1431
Block 4	150	162	110	675	699	1438	1134	1634	1656		1671	2345	2672	512500	1208

Table B.1-1: Porewater calcium concentrations (µg/L).

Reference

Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	2013-05-31	2013-07-09	2013-08-19	2013-09-27	2013-10-30
Block 1	22	34	24	42	56	55	37	66	64	56	52	62	99	183	83
Block 2	10	31	50	131	191	167	136	120	107	69	96	98	119	132	104
Block 3	5	7	6	24	26	24	26	16	20	16	16	17	18	15	18
Block 4	6	7	8	16	5	2	15	24	22		11	15	9	18	21

CFH-12&limestone

Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	2013-05-31	2013-07-09	2013-08-19	2013-09-27	2013-10-30
Block 1	10	8	8	9	10	6	6	139	8	8	7	7	8	8	6
Block 2	4	204	116	59	79	282	207	188	162	415	303	321	274	334	303
Block 3	6	5	2	5	4	5	5	11	10	3	3	5	4	4	4
Block 4	5	3	2	3	1	35	2	3	4		2	4	2	1	2

Zerovalent Fe

Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	41425	41464	41505	41544	41577
Block 1	5	3	1	1	2	1	1	16	3	3	2	1	2	1	1
Block 2	16	31	29	43	60	27	23	37	44	42	40	51	48	53	46
Block 3	30	4	2	1		2	1	4	7		1	2	2	2	1
Block 4	3	2	1	0	1	2	2	3	10		0	0	1	2	0

Table B.1-2: Porewater copper concentrations (µg/L).

Reference

Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	2013-05-31	2013-07-09	2013-08-19	2013-09-27	2013-10-30
Block 1	130	421	261	323	781	596	356	438	729	2145	515	711	737	841	333
Block 2	159	643	708	2710	1505	1146	1105	722	752	506	904	1194	1073	1066	731
Block 3	113	291	239	405	738	570	944	440	446	406	1088	1151	1952	361	214
Block 4	197	154	199	748	702	503	238	272	383		481	3142	2325	297	108

CFH-12&limestone

Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	2013-05-31	2013-07-09	2013-08-19	2013-09-27	2013-10-30
Block 1	37	49	870	31	152	33	122	58	56	64	118	295	278	113	35
Block 2	83	3754	2918	2126	2155	3972	3334	1980	2205	3337	2703	2725	2648	3316	2759
Block 3	150	78	17	49	275	155	80	73	82	43	230	313	208	125	34
Block 4	52	42	23	75	312	179	75	103	96		135	284	146	130	39

Zerovalent Fe

Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	2013-05-31	2013-07-09	2013-08-19	2013-09-27	2013-10-30
Block 1	80	251	133	52	626	213	347	445	665	1418	868	813	964	192	36
Block 2	135	335	342	1608	635	229	247	326	543	1159	523	5342	698	823	543
Block 3	140	225	103	176	309	283	343	995	1074		888	1857	1325	1685	52
Block 4	70	91	57	161	2109	331	251	209	269		266	1633	729	386	29

Table B.1-3: Porewater zinc concentrations (µg/L).

Reference

Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	2013-05-31	2013-07-09	2013-08-19	2013-09-27	2013-10-30
Block 1	192	365	307	582	838	715	435	794	270	631	482	730	866	1495	534
Block 2	93	429	782	1824	2870	2312	1608	1514	198	484	1299	1031	1024	1874	1319
Block 3	11	104	94	446	583	425	450	292	161	100	293	316	229	317	339
Block 4	7	52	65	123	195	214	104	110	56		103	394	32	37	63

CFH-12&limestone

Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	2013-05-31	2013-07-09	2013-08-19	2013-09-27	2013-10-30
Block 1	9	6	5	6	9	5	4	14	4	7	3	4	6	6	2
Block 2	16	1903	1118	1099	1526	2992	1388	1289	1529	2460	3308	2837	3250	3274	2727
Block 3	6	3	2	4	3	3	2	3	3	3	2	4	2	3	2
Block 4	5	2	1	2	1	2	1	2	1		1	1	1	1	1

Zerovalent Fe

Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	2013-05-31	2013-07-09	2013-08-19	2013-09-27	2013-10-30
Block 1	24	7	4	9	12	11	6	9	7	12	6	4	6	7	3
Block 2	139	360	415	845	778	269	241	301	545	171	402	485	737	664	636
Block 3	6	4	16	2		5	2	7	3		1	2	5	3	1
Block 4	2	1	1	1	2	1	2	2	1		1	0	1	3	0

Table B.1-4: Porewater lead concentrations (µg/L).

Reference

Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	2013-05-31	2013-07-09	2013-08-19	2013-09-27	2013-10-30
Block 1	349	308	132	214	291	297	185	229	269	195	277	305	264	260	128
Block 2	168	137	98	121	149	141	104	162	198	170	179	196	168	160	125
Block 3	202	118	98	102	144	174	118	144	161	114	157	150	170	119	115
Block 4	71	37	19	33	42	46	39	46	56		71	189	73	101	61

CFH-12&limestone

Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	2013-05-31	2013-07-09	2013-08-19	2013-09-27	2013-10-30
Block 1	80	80	68	96	120	76	82	106	124	69	108	123	102	121	88
Block 2	84	98	60	57	76	122	68	91	78	88	107	111	115	116	93
Block 3	33	33	19	35	44	47	29	37	44	20	36	48	47	46	30
Block 4	6	5	3	6	8	6	4	5	7		5	6	6	5	5

Zerovalent Fe

Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	2013-05-31	2013-07-09	2013-08-19	2013-09-27	2013-10-30
Block 1	81	80	47	63	113	79	58	54	83	38	51	72	67	55	32
Block 2	159	115	83	87	188	191	145	188	223	206	204	197	196	131	113
Block 3	36	20	20	15		58	50	42	42		36	56	55	81	31
Block 4	5	3	3	3	4	3	2	3	3		3	2	5	5	3

Table B.1-5: Porewater antimony concentrations (µg/L).

	Cu µg/L	Std	Zn µg/L	Std	Sb µg/L	Std	Pb µg/L	Std
SW 1	326	28	431	26	154	92	341	19
SW 2	665	488	359	237	284	206	841	654
SW 3	115	1	82	6	42	1	107	1
SW 4	222	4	96	6	92	1	199	5
Creek, upstream	7		30		1		0.5	
Creek, downstream	9		28		2		3	

Table B.1-6: Average surface water concentrations from four parts of the area in front of the stop butt and standard deviation (Std) from three replicates.

B.2 Saturation indices

	Saturation indices							
		Block 1			Block 2			Block 3
	Section	A	B	C	A	B	C	A
Ca	Aragonite	-4.16	-0.51	-3.50	-4.35	-2.30	-5.11	-4.67
	Ca-anitmonate	-3.13	-2.32	-5.15	-3.35	-2.26	-3.71	-3.93
	CaCO3xH2O(s)	-5.34	-1.70	-4.69	-5.54	-3.49	-6.30	-5.86
	Calcite	-4.00	-0.36	-3.35	-4.20	-2.16	-4.96	-4.53
	Dolomite (disordered)	-9.19	-2.37	-7.86	-9.29	-5.64	-10.83	-9.94
	Dolomite (ordered)	-8.58	-1.76	-7.31	-8.74	-5.09	-10.28	-9.39
	Portlandite	-16.99	-11.08	-14.26	-16.89	-13.88	-18.45	-17.21
	Vaterite	-4.61	-0.97	-3.92	-4.77	-2.72	-5.53	-5.09
Cu	Azurite	-10.80	-17.58	-18.70	-9.58	-6.70	-13.28	-13.84
	Cu(OH)2(s)	-6.17	-6.93	-7.81	-5.95	-4.35	-7.72	-7.37
	CuCO3(s)	-4.22	-7.23	-7.29	-3.66	-3.02	-4.63	-5.08
	Malachite	-7.05	-10.82	-11.84	-6.35	-4.11	-9.09	-9.19
	Tenorite(am)	-5.48	-6.24	-7.01	-5.15	-3.55	-6.92	-6.57
	Tenorite(c)	-4.63	-5.39	-6.16	-4.30	-2.70	-6.07	-5.72
Zn	Hydrozincite	-21.46	-9.15	-13.39	-23.17	-16.18	-29.20	-25.41
	Smithsonite	-2.84	-1.74	-2.20	-3.10	-2.27	-3.82	-3.54
	Zincite	-6.44	-3.08	-4.06	-6.72	-4.94	-8.25	-7.17
	Zn metal	-50.08	-51.05	-48.42	-47.57	-47.31	-47.68	-48.03
	Zn(OH)2 (am)	-7.65	-4.29	-5.30	-7.97	-6.19	-9.50	-8.42
	Zn(OH)2 (beta)	-6.91	-3.54	-4.58	-7.25	-5.47	-8.78	-7.70
	Zn(OH)2 (delta)	-6.23	-2.86	-4.67	-7.34	-5.56	-8.87	-7.79
	Zn(OH)2 (epsilon)	-6.65	-3.28	-4.36	-7.03	-5.25	-8.56	-7.48
	Zn(OH)2 (gamma)	-6.88	-3.51	-4.56	-7.23	-5.45	-8.76	-7.68
	Zn-Al LDH(s)	-9.35	-5.13	-6.40	-11.29	-6.27	-16.21	-12.81
	ZnCO3(s)	-2.91	-1.80	-2.30	-3.20	-2.37	-3.92	-3.64
	ZnCO3:1H2O(s)	-3.45	-2.34	-2.84	-3.74	-2.91	-4.46	-4.18
Pb	Cerrusite	-1.24	-4.40	-3.91	-1.20	-0.68	-2.25	-2.01
	Hydrocerrusite	-5.93	-13.15	-12.31	-5.93	-3.41	-9.89	-8.38
	Litharge	-8.64	-9.55	-9.53	-8.59	-7.11	-10.44	-9.40
	Massicot	-8.86	-9.76	-9.73	-8.79	-7.31	-10.64	-9.60
	Pb metal	-28.07	-33.31	-30.89	-26.43	-26.47	-26.86	-27.26
	Pb10(OH)6O(CO3)6(s)	-60.67	-83.21	-81.30	-61.21	-52.17	-74.94	-69.36
	Pb2O(OH)2(s)	-16.88	-18.68	-19.87	-17.98	-15.03	-21.69	-19.61
Sb	Sb2O5(s)	-11.55	-16.65	-15.10	-10.68	-12.59	-9.48	-10.94
	SbO2(s)	2.28	-2.43	-0.15	3.82	2.11	5.13	3.68

Table B.2-1: Saturation indices. Sampling day: 27-9-2013.

Reference

Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	2013-05-31	2013-07-09	2013-08-19	2013-09-27	2013-10-30
Block 1	117	102	298	180	277	61	52	125	69	185	43	41	137	116	82
Block 2	119	150	274	215	234	204	188	157	162		114	444	148	132	127
Block 3	261		161	181	238	105	58	183	200		77		75	79	62
Block 4		5	264	426		251	172		200						46

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Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	2013-05-31	2013-07-09	2013-08-19	2013-09-27	2013-10-30
Block 1	2925	3167	3581	2453	2499	2323	1668	1534	1454	1540	1380	2020	2147	1847	746
Block 2	435	2487	2176	1690	2337	2640	2174	1935	1555		2153	1344	2193	2773	2210
Block 3	3377	3406	3139		2662	2623	1962	2055	1617		1372		499		1511
Block 4	3703	3561	3606		2807	2812	2466	2016	1656		1725		2580	2280	2477

Zerovalent Fe

Date	2010-08-12	2010-09-17	2010-11-01	2011-05-28	2011-07-08	2011-09-01	2011-10-18	2012-06-13	2012-08-01	2012-10-24	2013-05-31	2013-07-09	2013-08-19	2013-09-27	2013-10-30
Block 1			176	274	78	76	36	125	60	140	19	9	20	20	17
Block 2	101	128	186	167	163	70	53	96	115		75		82	171	88
Block 3															
Block 4		23		590		75	59								14

Table B.3-1: Electric conducticity (µS/cm).